

AD-A011 723

CHEMICAL VAPOR DEPOSITION OF CADMIUM TELLURIDE

RAYTHEON COMPANY

PREPARED FOR

AIR FORCE MATERIALS LABORATORY

DEFENSE ADVANCED RESEARCH PROJECTS AGENCY

MARCH 1975

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

**Best
Available
Copy**

NO. 1001

Office of the Secretary
Department of Defense
Washington, D.C. 20304

NOV 1975

Final Report, 1 June 1973 - 31 January 1975

Approved for public release; distribution unlimited

Prepared for
DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
1400 Wilson Boulevard
Arlington, Virginia 22209

AIR FORCE MATERIALS LABORATORY
Air Force Systems Command
Wright-Patterson AFB, Ohio 45433

DDC
RESEARCH
PROJECTS
AGENCY

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. Department of Commerce
Springfield, VA. 22151

PRICES FOR 10 COPIES

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML-TR-75-68	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CHEMICAL VAPOR DEPOSITION OF CADMIUM TELLURIDE		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 6/1/73 - 1/31/75
7. AUTHOR(s) A. W. Swanson P. Reagan		6. PERFORMING ORG. REPORT NUMBER S-1836
9. PERFORMING ORGANIZATION NAME AND ADDRESS Raytheon Research Division 28 Seyon Street Waltham, Massachusetts 02154		8. CONTRACT OR GRANT NUMBER(s) F33615-73-C-5167
11. CONTROLLING OFFICE NAME AND ADDRESS Defense Advanced Research Projects Agency 1400 Wilson Blvd. Arlington, Virginia 22209		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project No. 2421/0002
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		12. REPORT DATE March 1975
		13. NUMBER OF PAGES 66
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Polycrystalline CdTe Chemical Vapor Deposition Laser Windows Long Wavelength 10.6 μ m		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Chemical vapor deposition techniques have been used to successfully deposit polycrystalline CdTe. The following two reactions were used to obtain theoretically dense material: $\text{Cd(v)} + \text{Te(v)} \rightarrow \text{CdTe(s)}$ $\text{Cd(v)} + \text{H}_2\text{Te(v)} \rightarrow \text{CdTe(s)} + \text{H}_2\text{(v)}$ Typical deposition temperatures ranged between 600° and 700° C.		

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

pressures varied from 10 to 40 torr, and the Cd(v)/ Te(v) molar input ratios were between 1.0 and 1.5.

The major problem encountered with the CdTe was the formation of physical voids in the material during the deposition process. Progress was made to limit the formation of these voids in the latter stages of the contract.

The in-line transmittance of the as-deposited CdTe approached the theoretical limit of 66% at 10.6 μm . Typical material was p-type with resistivities ranging up to 10^7 ohm-cm.

UNCLASSIFIED

ii SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

FOREWORD

This report was prepared by Raytheon Company, Research Division, Waltham, Mass., under Contract No. F33615-73-C-5167, ARPA Order No. 2421, Task 0002, Program Code No. 3D10, entitled, "Chemical Vapor Deposition of Cadmium Telluride." The work was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. Dr. Patrick M. Hemenger was project scientist.

The work was carried out at Raytheon Research Division, Advanced Materials Department. Dr. J. Pappis is the Department Manager. Dr. Alan W. Swanson was principal investigator. Experimental work was performed by Mr. Peter Reagan. Contributions to this investigation were made by Dr. T. Kohane and Mr. D. Howe.

This is the Final Technical Report for Contract F33615-73-C-5167. It covers the period 1 June 1973 to 31 January 1975. The report was given the Raytheon internal number S-1836.

The report was submitted by the authors 31 March 1975.

TABLE OF CONTENTS

	<u>Page</u>
I. INTRODUCTION AND TECHNICAL OBJECTIVE	1
II. ACCOMPLISHMENTS AND TECHNICAL DISCUSSION.....	3
A. Summary of Inherent Problems in Producing CdTe....	3
B. Cadmium Telluride State-of-the-Art	4
1. Fabrication.....	4
2. Optical properties.....	8
C. Chemical Vapor Deposition Process	12
1. Advantages	13
2. Static and dynamic CVD systems	13
3. Conventional and transport chemical vapor deposition	15
D. CVD of Polycrystalline CdTe	18
1. Summary.....	18
2. CVD system for CdTe	19
3. Evolution of mixing chamber and mandrel design	23
4. CVD of CdTe using metal-organics.....	34
5. CVD of CdTe using elemental Cd and Te	35
6. CVD of CdTe using elemental Cd and H ₂ Te gas ...	46
E. Physical Data	48
III. CONCLUSIONS	53
IV. FUTURE WORK	54
A. Introduction	54
B. Elimination of Internal Voids	54
C. Hardness and Strength Increase by Cation Additions.....	55
D. Hardness and Strength Increase by Precipitation Hardening	56
REFERENCES	57

LIST OF ILLUSTRATIONS

	<u>Page</u>
1 Phase Diagram for the Cadmium-Tellurium Binary System	6
2 Solid Stability Field of Cadmium Telluride	7
3 Frequency Dependence of Optical Loss in Chalcogenide Materials	9
4 Typical Data for Absorption vs Thickness in ZnSe. Extrapolated values of surface loss range from a minimum of 0.0003 per surface	11
5 Typical ZnSe Plate Made by CVD Process	14
6 Schematic Drawing of CVD Zinc Selenide Apparatus	16
7 System for CVD of Cadmium Telluride	20
8 Schematic of CVD System for CdTe	21
9 Schematic of Redesigned Furnace Deposition Chamber	22
10 Initial Deposition Setup With Circular Mandrel	25
11 Deposition Chamber with Concentric Reactant Inlets	26
12 Mandrel Configuration Used With H_2Te and Dimethyl Tellurium	27
13 Mandrel Design Incorporating a Circular Mixing Chamber and a Deflection Plate in the Mandrel Area	29
14 Set-up With Reactant Inlets Perpendicular to the Normal Flow	30
15 Deposition Set-up With Mandrel Perpendicular to Gas Flows	31
16 Design Using a Venturi-Type Mixing Chamber and A Vertical Mandrel	32
17 Design Using a Six-Sided Mandrel	33
18 In-Line Transmittance of Run CdTe-15	41
19 Temperature Profile of Furnace Used to Allow Supersaturation of the Reactants to Occur in the Mandrel Area	43

List of Illustrations (Cont'd)

		<u>Page</u>
20	In-Line Transmission of CdTe-54, Thickness = 0.020 in.	44
21	In-Line Transmission of CdTe-58, Thickness = 0.100 in.	45
22	Voids in As-Deposited Polycrystalline Cadmium Telluride Run CdTe-71 (100X)	49
23	In-Line Transmittance from the Visible to 40 μ m, CdTe-100	50

I. INTRODUCTION AND TECHNICAL OBJECTIVE

Former research and development efforts have established that cadmium telluride (CdTe) is a promising material for use as high power laser windows, electro-optic modulators¹, and as gamma-ray detectors.^{2, 3} For the latter applications single crystals are needed, while for laser windows, both single crystal and polycrystalline material are usable. In the fabrication processes used prior to this work difficulties were experienced in controlling the structural perfection and purity of the material, and as a result, the use of the material has been rather limited. The chemical vapor deposition process offers the promise of overcoming some of the difficulties experienced to date. Thus, the primary objective of the program was to establish the technology base that would allow one to determine the usefulness of the process.

The program was of 18 months duration and was carried out in several phases. The first phase involved the investigation of several processes for the CVD of CdTe. The specific processes investigated and evaluated were: 1) dimethyl cadmium and dimethyl tellurium vapors; 2) dimethyl cadmium and tellurium metal vapors; 3) dimethyl cadmium vapor and H_2Te gas; 4) cadmium metal and dimethyl tellurium vapors; and 5) Cd and Te vapors; and (6) H_2Te gas and Cd vapor.

The second phase involved the task of process optimization. The most promising methods yielding satisfactory material under the first phase were studied more thoroughly. The process parameters which were determined to be of importance were: deposition temperature, furnace pressure, and molar ratio of the reactants.

The third phase of this program ran concurrently with the first two phases. It involved the evaluation and measurement of the various process parameters such as deposition rate and profile, as well as quantitative and qualitative determinations concerning the structure and properties of CdTe. The material was characterized optically using infrared transmission. Laser

calorimetry was used to determine the absorption coefficient of CdTe at 10.6 μm . Properties such as microhardness were studied to determine the effect of various deposition conditions on the mechanical properties of the material. The results of these studies indicate that the chemical vapor deposition process can yield theoretically dense cadmium telluride. Furthermore, the results indicate that it will be feasible to fabricate an improved state-of-the-art material using this process.

II. ACCOMPLISHMENTS AND TECHNICAL DISCUSSION

A. Summary of Inherent Problems in Producing CdTe

Detailed studies on the growth and properties of synthetic CdTe have been in progress since 1955, although interest in the growth of large, single crystals with a high $\mu\tau$ product for gamma-ray detectors did not occur until 1966. The most recent emphasis on production of large, low-loss, low-scatter optical components is part of the development of high power 10.6 μm laser systems. In 1966, CdTe was introduced as an infrared window material in the form of a hot pressed polycrystalline aggregate.* This form, which is adequate for use in passive infrared systems, is far from satisfying the more stringent laser requirements.

In principle, the material properties required in an infrared window should be attained more easily than those called for in high-resolution gamma-ray detectors. In the latter case the utility of the material is affected by charge transport properties and is sensitive to both intrinsic and extrinsic lattice and crystal defects on an atomic scale. Defect and impurity-induced free-carrier concentrations at room temperature are typically $1 \sim 5 \times 10^{14}/\text{cc}$ in the most pure material. By deliberate compensation techniques, this level can be dropped to $\sim 10^7/\text{cc}$, but this merely tends to change the level of conductivity without improving the $\mu\tau$ product. For windows, however, the predicted free carrier absorption intensity at 10.6 μm for n-type material with a carrier concentration $1 \times 10^{14}/\text{cc}$ is 0.02 cm^{-1} . Thus, a reduction of carrier concentration by a factor of only 10^2 would result in a bulk loss coefficient of 0.0002 cm^{-1} , less than the present state-of-the-art of 0.0006 cm^{-1} measured on semi-insulating material with apparent free carrier concentrations less than $10^{10}/\text{cc}$. Furthermore, the extrapolated multiphonon loss curve predicts an intrinsic bulk absorption coefficient of 10^{-8} cm^{-1} at 10.6 μm and should be of not practical significance

* Kodak's Irtran 6

In all probability, low-loss CdTe is difficult to achieve because of material nonuniformity, both in impurity concentration and in the generation and subsequent segregation of native defects, which can cause localized conductive and absorptive regions in an apparently high-resistivity material, or precipitated metallic particles and voids that act as scatter centers. Impurity and defect suppression in crystals grown from the melt, or by condensation at high temperatures, is difficult to achieve.⁴ Chemical vapor deposition (CVD) offers the one technique wherein theoretically dense material can be produced at temperatures well below the melting point, and where surface migration is relied upon to give pore-free material.

B. Cadmium Telluride State-of-the-Art

1. Fabrication

Although experiments on synthetic cadmium telluride were initiated in the early 1950's, the first comprehensive study of the metallurgical and electronic properties of this material was reported by D. deNobel in 1959.⁵ In addition to studying the temperature-composition and pressure-temperature projections of the binary phase diagram, he made resistivity and Hall-coefficient measurements on doped and nominally-undoped single crystals which had been quenched after being annealed over a range of temperatures and cadmium partial pressures. On the basis of this work and much subsequent work it has been shown that CdTe can undergo stoichiometric deviations when grown at high temperatures, and that such changes in composition are caused mainly by lattice defects which determine the level of conductivity and carrier type. A recent analysis of the state-of-the-art in CdTe single crystals has been published by Strauss.⁴

The two main processes that have been used to fabricate high quality CdTe single crystals (and in some cases polycrystals) are growth from a liquid-phase and growth from the vapor phase. Of the two processes liquid phase growth has been most extensively used. This is not surprising because

of its relative simplicity, rapidity and reliability for a material that melts congruently at accessible temperatures (Figure 1). In the case of liquid growth material, growth is initiated at 1092° C, then a temperature gradient is established across the melt and swept through it in order to cause directional crystallization. Growth from the vapor phase, on the other hand, is normally carried out at temperatures between 1020° and 1050° C. In conventional vapor deposition, CdTe or elements of the compound after purification and sintering are sublimed or evaporated and transported to a cooler portion of the furnace where they are condensed on an appropriate substrate.

The high temperatures involved in both processes cause substantial concentrations of native vacancies to form because the composition deviates from its stoichiometric value. In cadmium telluride cation vacancies predominate over anion vacancies. The equilibrium concentration of vacancies is a function of temperature, composition of the equilibrium gas, and the concentration of foreign donors and acceptors. As the crystal is cooled (both processes) the allowed range of deviation from the stoichiometric composition decreases as given by the solid-solubility field of the phase diagram (Figure 2). Precipitation of the major vacancies occurs because the vacancies of the bulk crystal cannot be cooled rapidly enough to quench them; therefore, the majority of vacancies cluster at nucleation points within the host lattice. Because the minority host atoms have no place to escape they remain within the same volume of the condensed vacancies.

In CdTe, cadmium vacancies condense with an equal number of tellurium atoms, forming voids that are partially filled with elemental tellurium. The formation of vacancies can be suppressed by imposing a sufficiently high pressure of the element corresponding to the majority vacancy at the growth temperature. In the case of vapor deposition this results in the suppression of sublimation so that reasonable growth rates cannot be attained. Slow cooling results in the formation of a relatively small number of large precipitates while fast cooling results in a larger number of small precipitates; the total volume of the precipitates is approximately equal in both cases. The

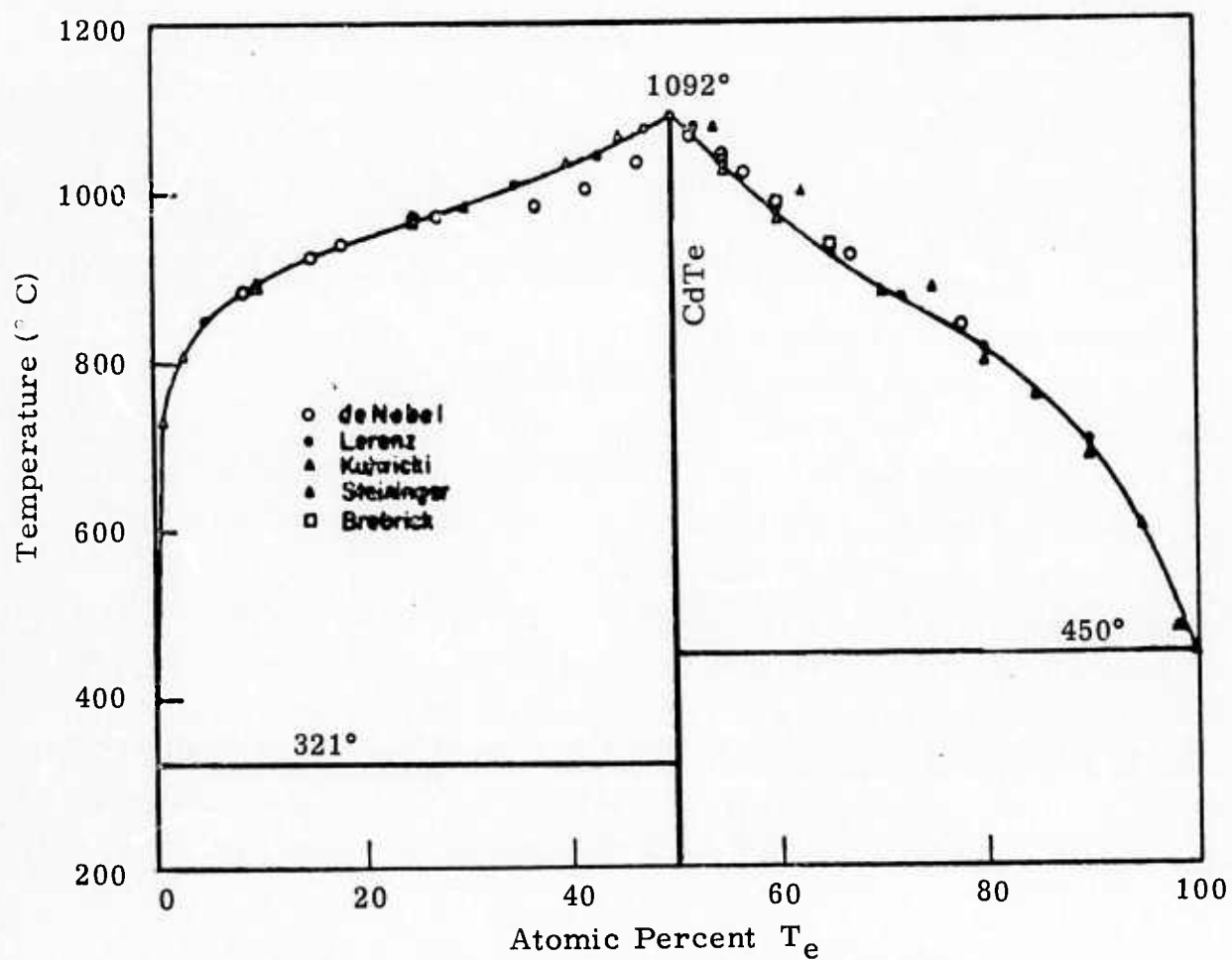


Figure 1. Phase Diagram for the Cadmium-Tellurium Binary System

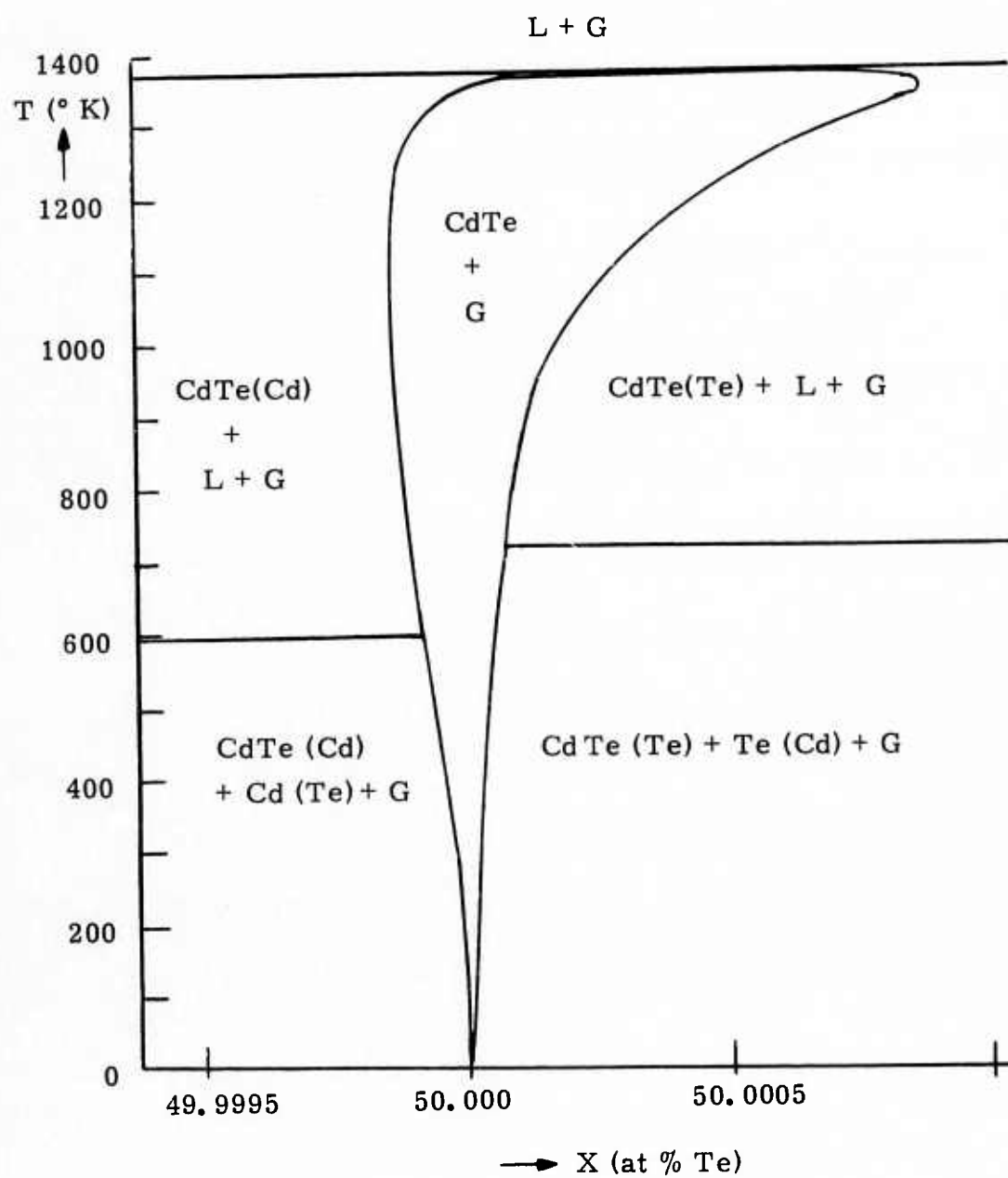


Figure 2. Solid Stability Field of Cadmium Telluride

effect of precipitates on optical properties can be minimized after growth, by reheating the material and equilibrating it with respect to a controlled partial pressure of the proper element. Alternatively, a proper dopant can be added to the melt or vapor to compensate the precipitant.

2. Optical properties

Cadmium telluride in high-resistivity form is essentially transparent between the (indirect) electronic edge at 1.39 eV (0.89 μm) and the multi-phonon edge near 23 μm . The refractive index at 10.6 μm is 2.67, and results in a two-surface incoherent reflection loss of 34 percent.

The recognition, or rediscovery, by Deutsch⁶ and others that the multiphonon absorption edge can be described empirically as an exponential function of frequency

$$\beta = \beta_0 e^{-\nu/\nu_{10}}$$

where ν_{10} is the frequency associated with the longitudinal optical lattice mode, allows us to predict the corresponding absorption at 10.6 μm for the II-VI chalcogenides.

The situation is summarized in Figure 3. The data collected for ZnSe, CdTe, GaAs in the range of measurement (β values between 0.5 and 100 cm^{-1}) have a very similar form when plotted on the reduced frequency scale ν/ν_{10} . The data for CdS and ZnS, although not plotted in this figure, virtually superpose on these curves. We estimate the enveloping exponential line to pass through the CdTe, 10.6 μm point at $\beta \approx 10^{-8} \text{ cm}^{-1}$. This figure is so low that it is unlikely ever to be measured directly.

Information on free carrier absorption⁹ shows that it depends on wavelength approximately as λ^3 in this spectral range (at least at room temperature and above). The data for an n-type carrier concentration of

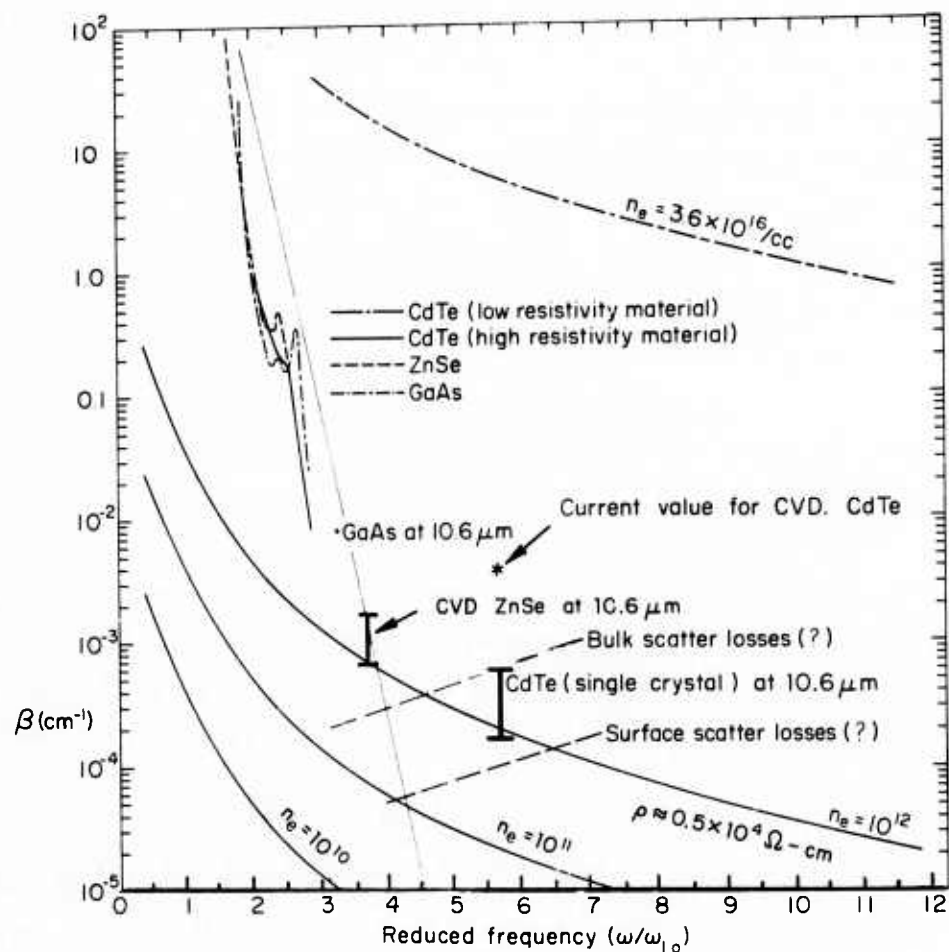


Figure 3. Frequency Dependence of Optical Loss in Chalcogenide Materials

$3.6 \times 10^{16} / \text{cc}$ is indicated on the figure, along with the estimates derived from this data for samples of low carrier concentration. Electron mobility at room temperature is approximately $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in high-quality single crystals, implying that the carrier concentration for a typical n-type semi-insulating crystal with $\rho = 5 \times 10^7 \text{ ohm-cm}$, is $10^8 / \text{cc}$. Such a material should give a free-carrier absorption at $10.6 \mu\text{m}$ of $2 \times 10^{-8} \text{ cm}^{-1}$. The state-of-the-art CdTe loss coefficient measured calorimetrically at $10.6 \mu\text{m}$ is $\sim 0.0006 \text{ cm}^{-1}$. Therefore, resistivities of no more than 3000 ohm-cm would suppress the free carrier loss to this level; in fact, this loss data was taken on semi-insulating material with apparent resistivities above 10^6 ohm-cm .

Another possible source of loss is scattering. Calorimetry on ZnSe (Figure 4) material shows that loss for conventionally polished surfaces is typically in the range 0.0001 to 0.0003 per surface. In ZnSe, this figure is more likely to be derived from a scatter and reabsorption process than from a direct absorption, although water and organic-film contamination is also possible. In any case, the CdTe loss figure for a 1 cm sample is approaching the anticipated surface loss. The practical limit for these losses must be considered. Super-polishing of surfaces may well drop the surface loss by an order of magnitude, to 10^{-5} per surface, and is the subject of current research initiatives. To reach this level of bulk loss in a 1 cm sample will require uniform resistivity material with $\rho > 10^5 \text{ ohm-cm}$. The material must also be free of internal metallic particles or voids that can act as scatter centers.

For particles much larger than the operative wavelength, the scatter cross-section of imbedded particles is equal to their geometric cross-section. This is not much different for particles greater than $\sim 2.5 \mu\text{m} (\lambda / 4)$ in minimum dimension. This means that for CdTe at $10.6 \mu\text{m}$, particles bigger than $1 \mu\text{m}$ can be considered large in this context. A volume concentration of 1 ppm of opaque scatterers $1 \mu\text{m}$ in size would produce a scatter coefficient of approximately 10^{-2} cm^{-1} , while the same volume concentration of $10 \mu\text{m}$ particles

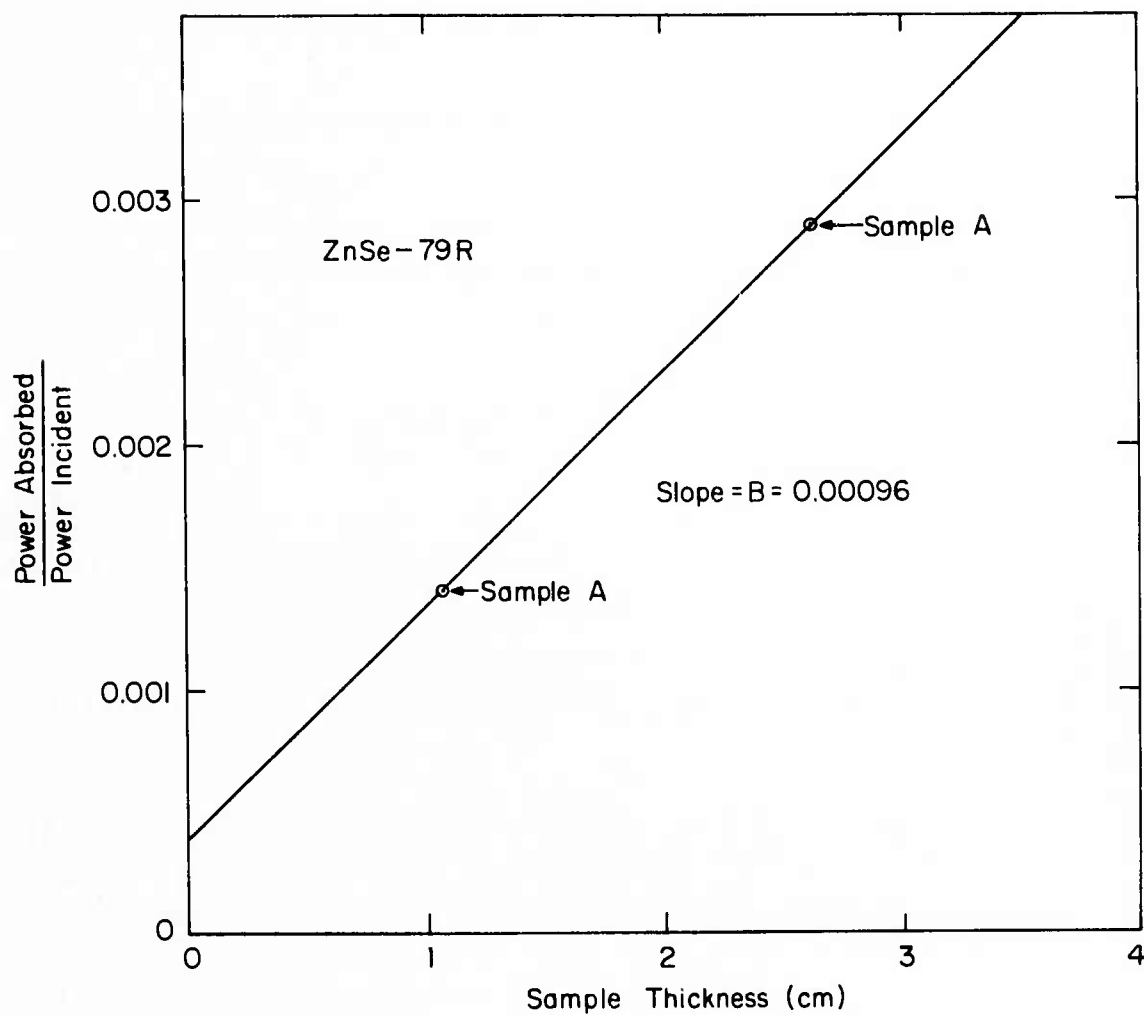


Figure 4. Typical Data for Absorption vs Thickness in ZnSe. Extrapolated values of surface loss range from a minimum of 0.0003 per surface.

would give $\beta_{\text{scatt}} \approx 10^{-3} \text{ cm}$. It follows that the observed loss factor of $0.6 \times 10^{-3} \text{ cm}^{-1}$ could be explained by a fractional reabsorption of the scatter from 100 parts per billion of particulate matter, voids, or high-conductivity grains $1 \mu\text{m}$ in size.

Experiments at Tyco⁸ to determine the influence of CdCl_2 additions on loss at infrared wavelengths showed an easily detectable loss spectrum at wavelengths as short as $4 \mu\text{m}$ for chloride concentrations in excess of 10 11m. Their explanation of this increased loss in terms of chloride vibrational absorption is unconvincing. In fact, the spectrum is close to the λ^3 dependence expected for free carriers, and is almost certainly due to isolated conducting regions. The apparent resistivity of 10^6 ohm-cm or greater in these samples must be explained on the basis either of isolated conductors immersed in a high resistivity matrix, or as the I/V characteristic of a multitude of back-biased p-n diodes produced by compositional changes or fluctuation in impurity or defect density throughout the matrix. These possibilities emphasize the need for high-sensitivity loss or calorimetry measurements as a function of wavelength to attempt to distinguish between scatter losses, free-carrier losses, or impurity vibrational losses in low-loss CdTe material.

C. Chemical Vapor Deposition Process

The concept of the CVD process is quite easily understood; volatile compounds or other volatile species of the material to be deposited are passed into the deposition zone of a furnace which has been heated to some predetermined temperature and is held at some predetermined pressure. (For example, a typical deposition temperature for CdTe is 600°C and the furnace pressure is 20 torr.) The volatile compounds are directed to the substrate and are then allowed to thermally decompose and react at the substrate to form the solid material. Typical deposition rates are 0.005 to 0.010 in/hr. The reaction products are pumped away and disposed of by some suitable method.

The CVD process as described, with minor modifications, has been used to fabricate many materials over the past ten to fifteen years. Among the materials fabricated are pyrolytic graphite, boron nitride, alumina, zinc sulfide, cadmium sulfide and zinc selenide. Figure 5 shows a typical ZnSe plate made by this process.

1. Advantages

Chemical vapor deposition offers many advantages over more conventional processes for preparing infrared materials. Perhaps the most significant of these can be summarized as follows:

- a) The equipment needed is relatively inexpensive, and size and thickness of required materials are not serious limitations.
- b) Both simple and complex shapes can be fabricated with relative ease.
- c) The density and purity of the material is usually very high, thus scatter and impurity absorptions are minimized.
- d) Since deposition occurs at temperatures one-third to one-half of the melting or sublimation point of the compound, stoichiometry is usually not a serious problem.

2. Static and dynamic CVD systems

Two general types of systems, static and dynamic, can be used for chemical vapor deposition. The static system is a closed system, in which the reactants and products are sealed in a chamber. Well-known examples are the quartz-iodine incandescent lamp and the hydrothermal bomb for the deposition of synthetic quartz. In the dynamic system, on the other hand, fresh reactants are continuously metered into the deposition chamber, and

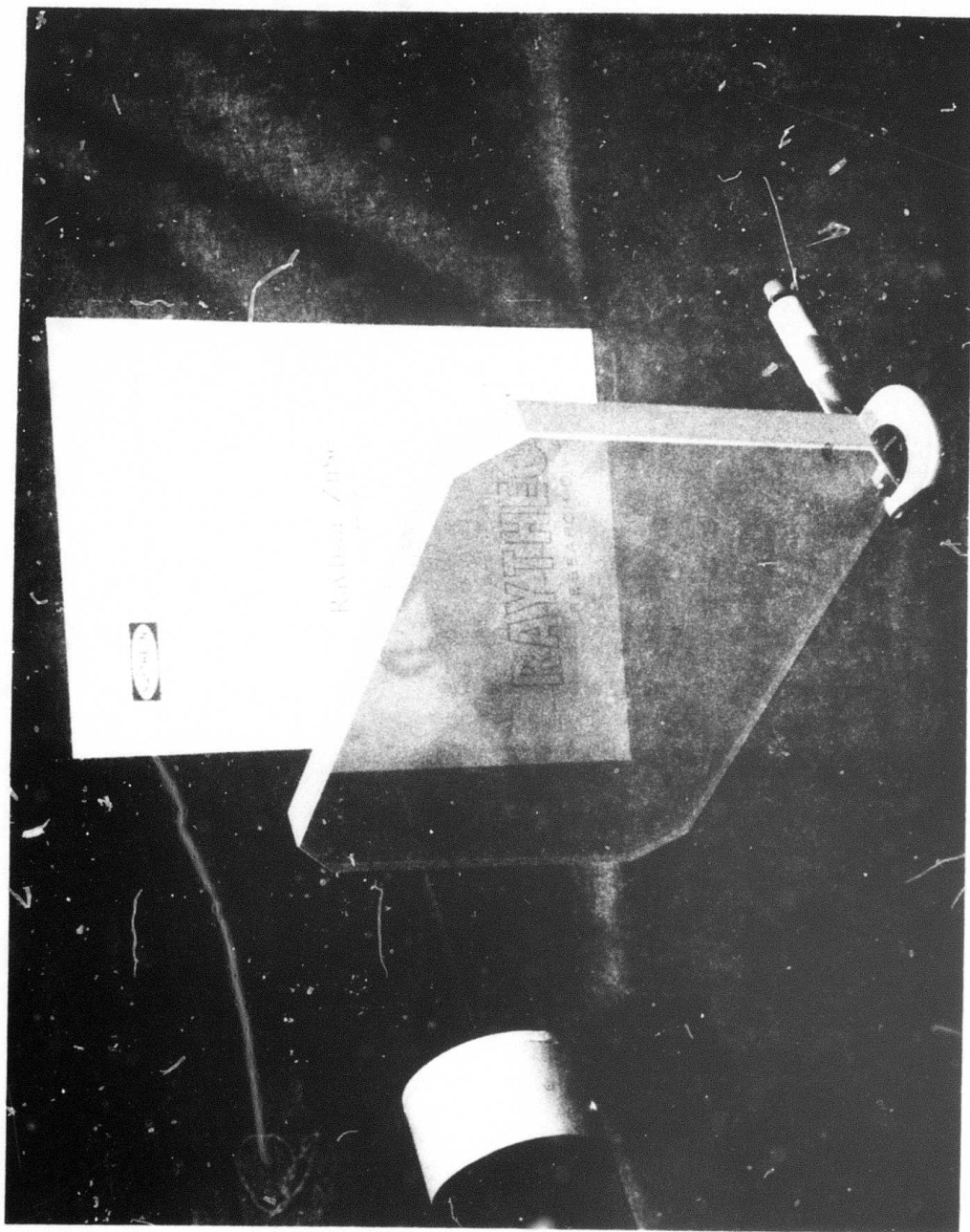


Figure 5. Typical ZnSe Plate Made By The CVD Process

the spent vapors are continuously removed, usually by pumping. Figure 6 is an example of a simple dynamic CVD system. The reactive gases are fed into the furnace through a gas-metering system. The substrate upon which the deposit occurs is maintained at an appropriate temperature by means of a heater that is inductively or resistively heated. Most vapor depositions are made at pressures on the order of one-hundredth of an atmosphere, although a much higher or lower pressure can be employed.

Our experiments have shown that the dynamic system yields good results in the deposition of cadmium telluride, zinc sulfide, and zinc selenide, and is preferable because it offers certain advantages over the static systems. Chief among these is the depletion of reactants and the accumulation of waste materials which are major problems in the static system, whereas the dynamic system allows the addition and removal of materials during deposition thus minimizing these problems. In order to obtain a deposit, the temperatures of the substrate chamber and the vapor source are usually more critical and interdependent in the static system than in the dynamic system. The static system, in general, offers less flexibility in the deposition parameters than the dynamic system, since vapor transport is controlled by temperature gradients rather than pressure gradients and mass flow. In addition, the static system is often more susceptible to vapor-phase nucleation and particle growth near the substrate; to reduce this effect the partial pressures of the reactive vapors must be low, resulting in low deposition rates. The reactive-vapor concentrations are also limited by the equilibrium constants of regenerative reactions and by the fact that partial pressures of the regenerative vapor cannot (for safety reasons) usually greatly exceed one atmosphere. Finally, outgassing of deposition chamber and substrate are of greater importance in the static system than in the dynamic system.

3. Conventional and transport chemical vapor deposition

Two general techniques can be employed in vapor deposition. These are: 1) Conventional chemical vapor deposition where the vapor source

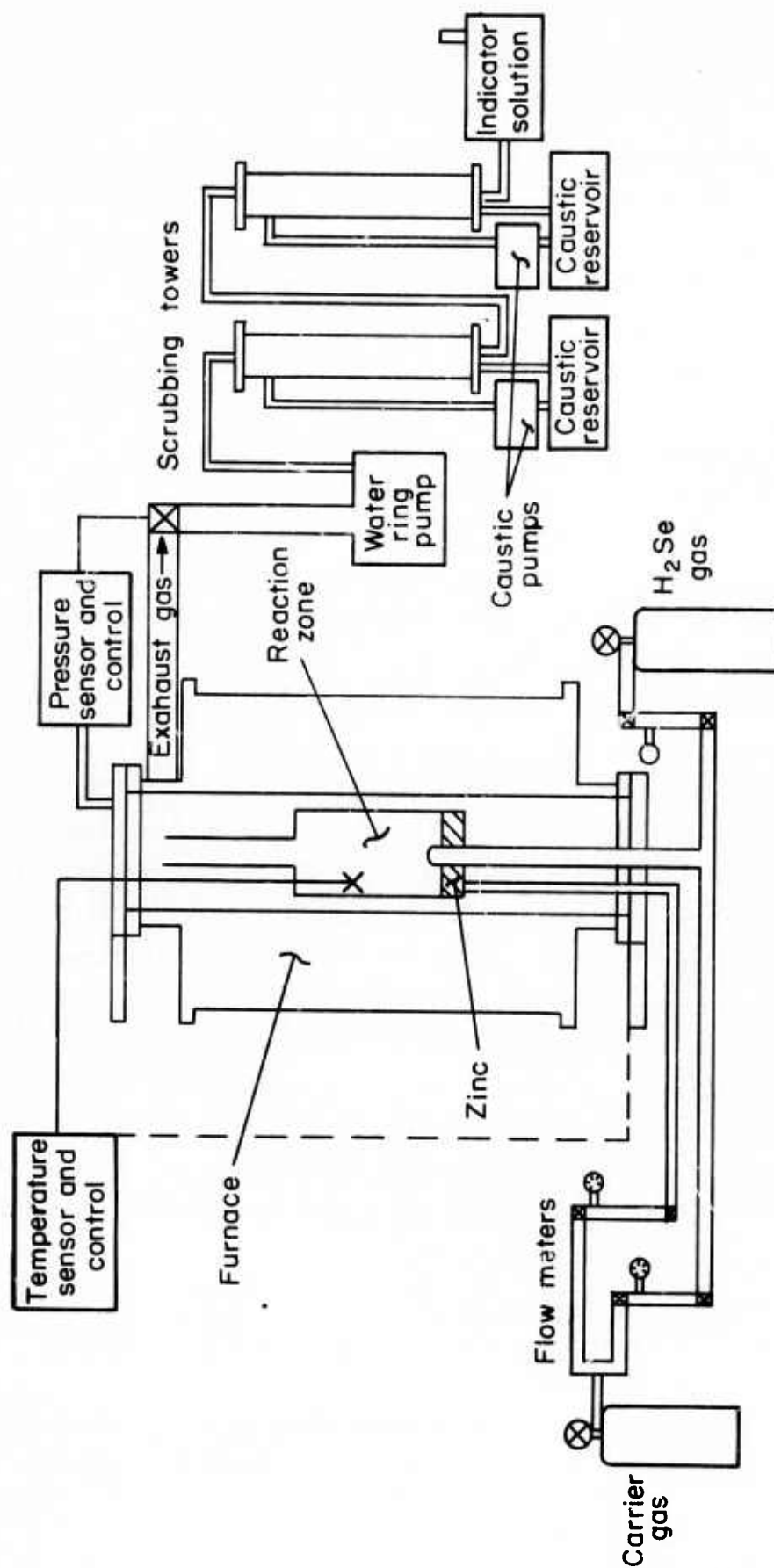


Figure 6. Schematic Drawing of CVD Zinc Selenide Apparatus

temperature is lower than the substrate temperature; 2) Transport chemical vapor deposition,⁹ where the vapor source temperature is greater than the substrate temperature.

In conventional chemical vapor deposition, the thermodynamics and kinetics of the chemical reactions are such that formation of the solid product is favored at the higher temperatures, whereas the volatile reactants tend to be formed or are stable at the lower temperatures.

In chemical-transport deposition, on the other hand, the thermodynamics and kinetics of the chemical reactions are such that formation of the solid product is favored at the lower temperatures, whereas the volatile reactants are formed at the higher temperatures.

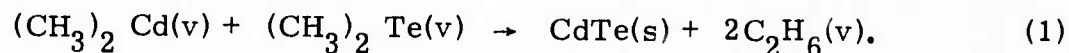
The initial experiments at Raytheon employed chemical transport deposition in a dynamic system using HCl to transport zinc sulfide. It was soon discovered that conventional chemical vapor deposition in a dynamic system yielded superior results, and this method has been used for the deposition of ZnSe and CdTe at the Research Division.

D. CVD of Polycrystalline CdTe

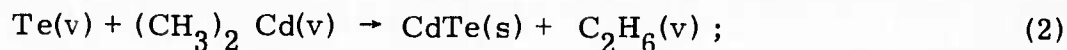
1. Summary

Initially, six different chemical reactions were proposed as possible methods for the CVD of cadmium telluride.

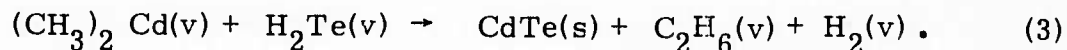
The first four possible reactions involved various combinations of organo-metallic compounds, cadmium or tellurium metal, and hydrogen telluride gas. The first method combined dimethyl tellurium and dimethyl cadmium to form CdTe in the reaction:



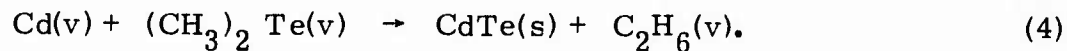
As an alternative, dimethyl cadmium and tellurium vapor could be combined according to the following reaction:



or a combination of dimethyl cadmium with H_2Te gas could be used in the reaction:



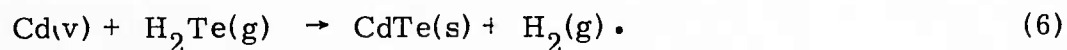
Finally, dimethyl tellurium and cadmium vapor could be used in the reaction:



In addition to the reactions listed above, there are two other possible methods of producing polycrystalline CdTe. The first involves combining Cd and Te metal vapors in the reaction:



The last reaction is an analog of the reaction used to successfully deposit zinc selenide. Cadmium vapor and H_2Te gas could be combined in the following manner:



The standard free energy of reaction for the six deposition methods listed above falls between -2 and -10 Kcal/ mole. The free energy of reaction for ZnSe under normal deposition conditions is ~ -22 Kcal/ mole. Thus, it was felt that from a free energy point of view it should be possible to deposit polycrystalline CdTe from one of the above reactions.

2. CVD system for CdTe

Since the main goal of this contract was to find one or more methods of producing polycrystalline CdTe by the CVD process, it was determined that a large number of experimental runs of fairly short duration would have to be made. For this purpose the small CVD system pictured in Figure 7 was built. A schematic of the same system is shown in Figure 8. By using a small deposition furnace many more runs can be made, and thus much more information can be gained, for the same materials cost.

The system consists of a flow panel pictured on the left. The flowmeters are used to control the carrier gas flow over the liquid metal retort or over the organo-metallic compounds in the bubbler systems. One of the flowmeters also controls the amount of H_2Te gas passing into the furnace through the nozzle system. The pressure gages for the system are also located on this flow panel.

The reaction chamber consists of a graphite retort, mixing chamber, and mandrel. A schematic of the setup is shown in Figure 9. Any gases are brought into the mixing chamber via a stainless steel nozzle. If two gases

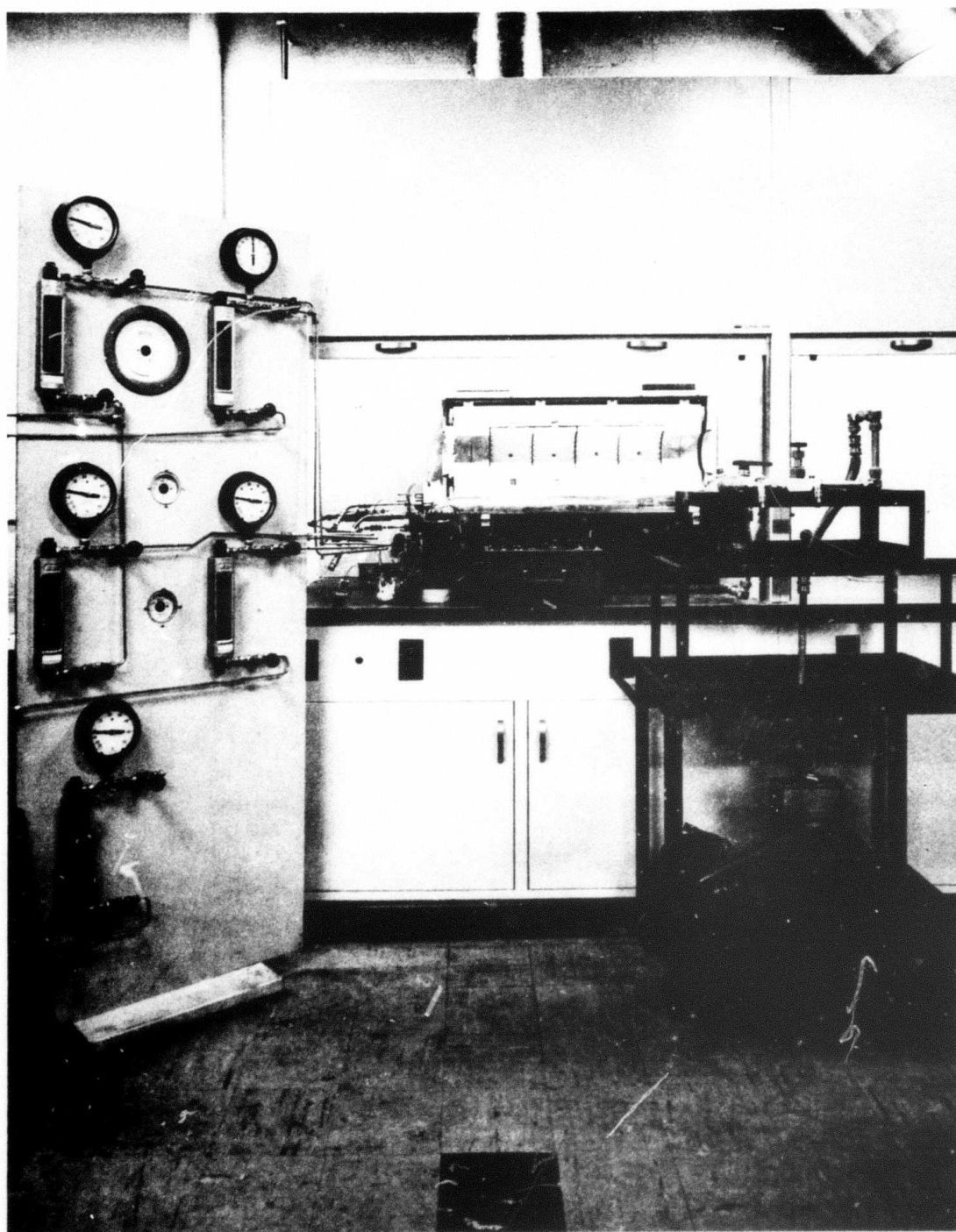


Fig. 7 System for CVD of Cadmium Telluride

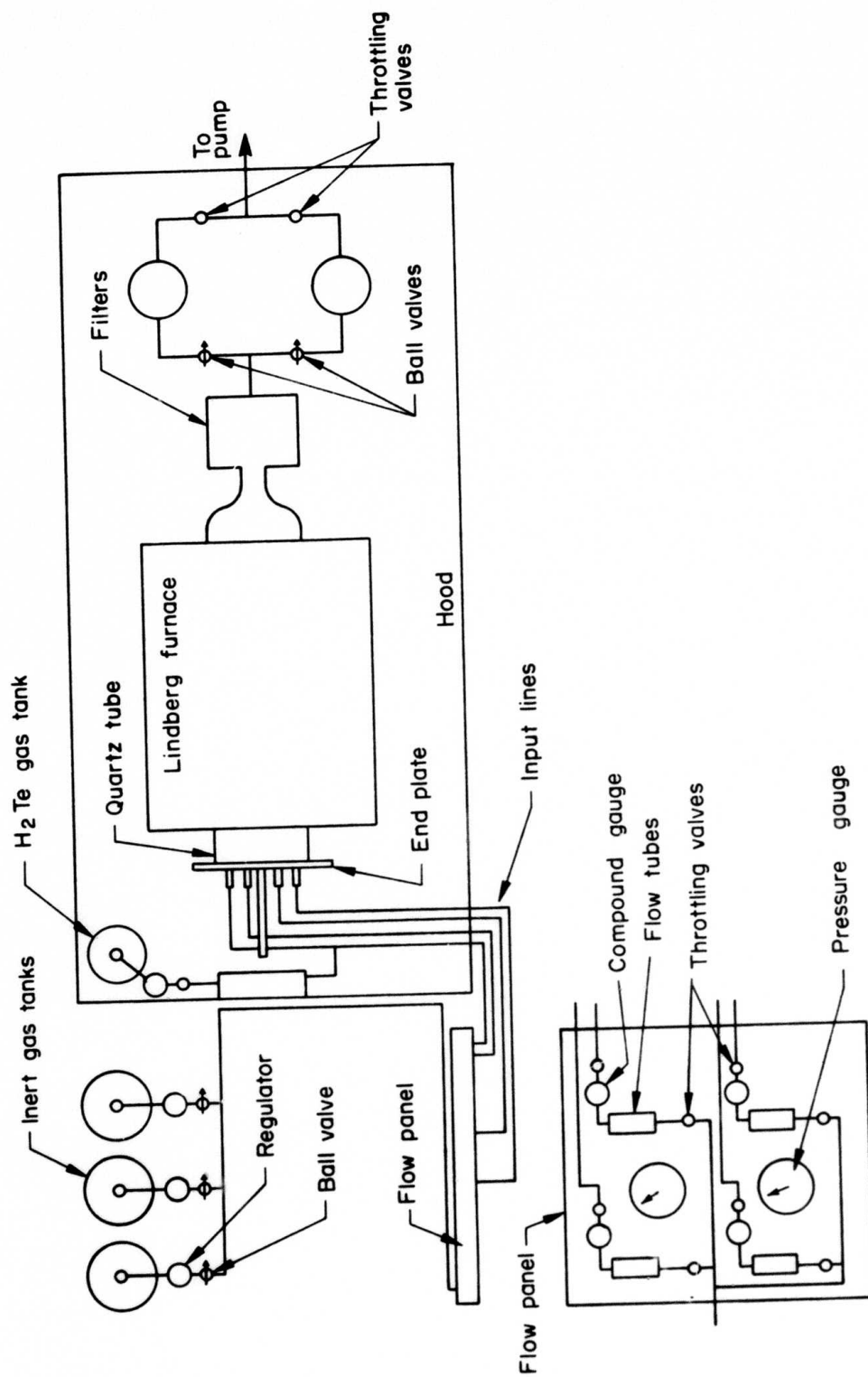


Figure 8. Schematic of CVD System for CdTe

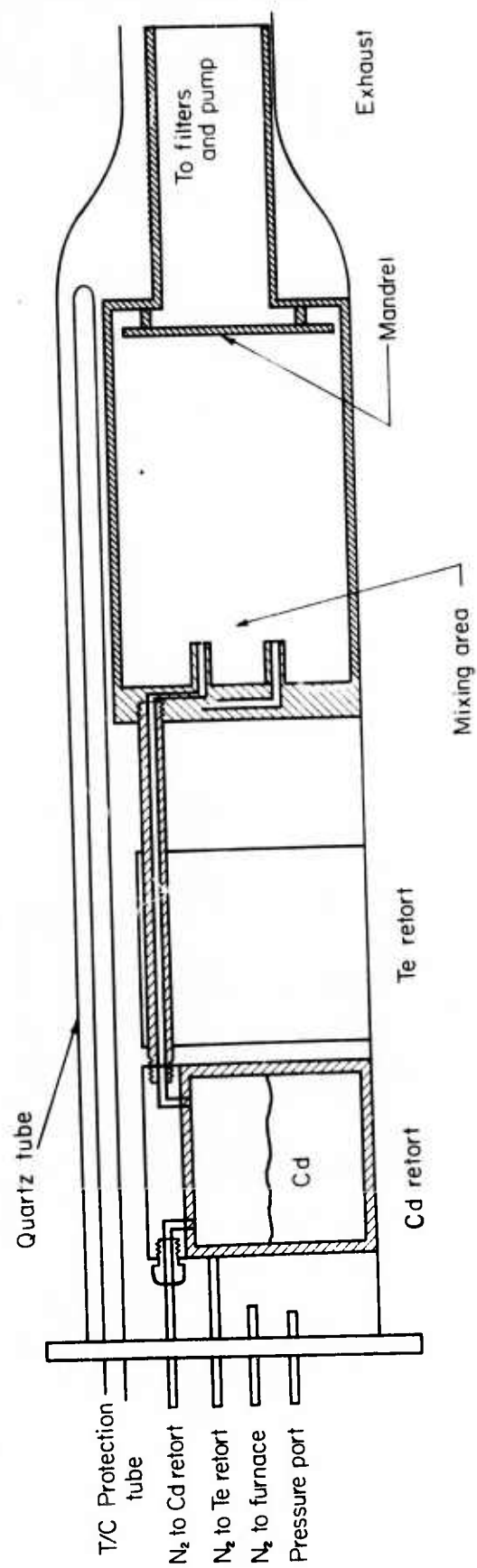


Figure 9. Schematic of Redesigned Furnace Deposition Chamber

or vapors are to be introduced into the mixing chamber, the retort containing the metal is merely replaced by another nozzle.

The reaction chamber is heated by a Lindberg 4-zone furnace which is 5 in. in diameter (Figure 7). Each 6-inch zone has an individual controller so that temperature gradients along each zone can be controlled to within $\pm 0.5^\circ \text{C}$. The furnace and reaction chamber are housed in a 10 ft. exhaust hood for safety purposes.

The vacuum and exhaust system is shown to the right in Figures 7 and 8. It consists of a dust filter, throttling valve, and a vacuum pump. The exhaust from the pump is then passed through KOH bubblers to neutralize any harmful vapors.

At the beginning of the program a considerable amount of time was spent in designing and redesigning the above system so that it would run efficiently. While the graphite mixing and mandrel designs (Figure 9) have been modified from run to run, the basic CVD system has not been changed since run CdTe-30.

3. Evolution of mixing chamber and mandrel design

When trying to deposit a material in a crystalline form, determining the design of the reactant mixing chamber and mandrel area is as important as determining the proper reaction to be used. As the various CdTe runs were carried out, different configurations for the deposition were tried and were either accepted or rejected.

The following sketches show most of the major mandrel configurations used in developing the ability to deposit CdTe. The various designs were fabricated from ATJ graphite.

The first setup used for the first ten process runs is shown in Figure 10. On runs 1 thru 4 there was no baffle plate used, and the inlets fed the reactants directly into the mandrel. A baffle plate was used in runs 5 thru 10 with the goal of initially mixing the Cd and Te vapors more thoroughly. Polycrystalline CdTe was deposited during several of the runs mentioned above, but it was deposited at random throughout the mixing chamber and mandrel rather than on the walls of the mandrel.

Figure 11 shows the second configuration used to deposit material. Concentric Cd and Te vapor inlets were used in an effort to achieve uniform mixing of the reactants. Again the CdTe did not deposit uniformly on the walls of the mandrel. Instead, ribbon-like deposits of CdTe were formed from the reactant inlets to the exhaust area of the system.

For CdTe runs 14 thru 16 the setup was essentially the same as that already shown in Figure 10. Only one inlet hole for each reactant was used, however. A layer of CdTe was deposited on the back side of the baffle plate only.

The mandrel design shown in Figure 12 was used on runs 17 thru 23 and on runs 31 thru 35. In the first series of runs dimethyl tellurium and cadmium vapor were used as reactants. No crystalline CdTe resulted from CdTe runs 17 thru 23. In the second series of runs using this mandrel design hydrogen telluride gas was fed in through the center opening with Cd vapor coming in the other two openings. A thin layer of polycrystalline CdTe was deposited through most of the mixing chamber and mandrel areas.

Runs 24 thru 30 were made using Cd and Te vapors as reactants and the basic design configuration shown in Figure 10. The position of the inlets and baffle plate were varied from run to run in an attempt to obtain an even deposit of CdTe on the mandrel. Only ribbon-like structures of CdTe filled the deposition area however.

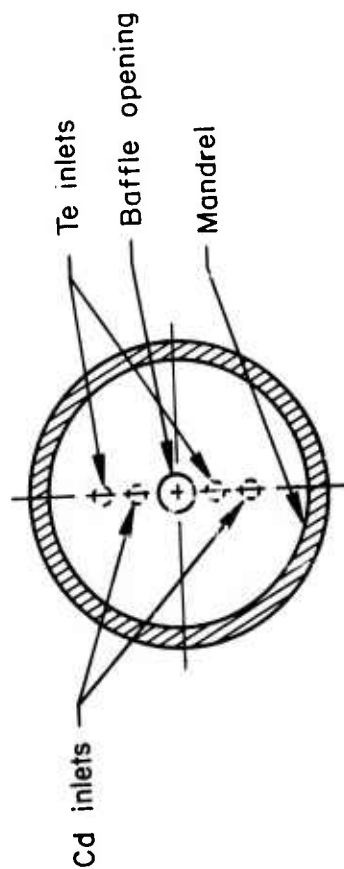
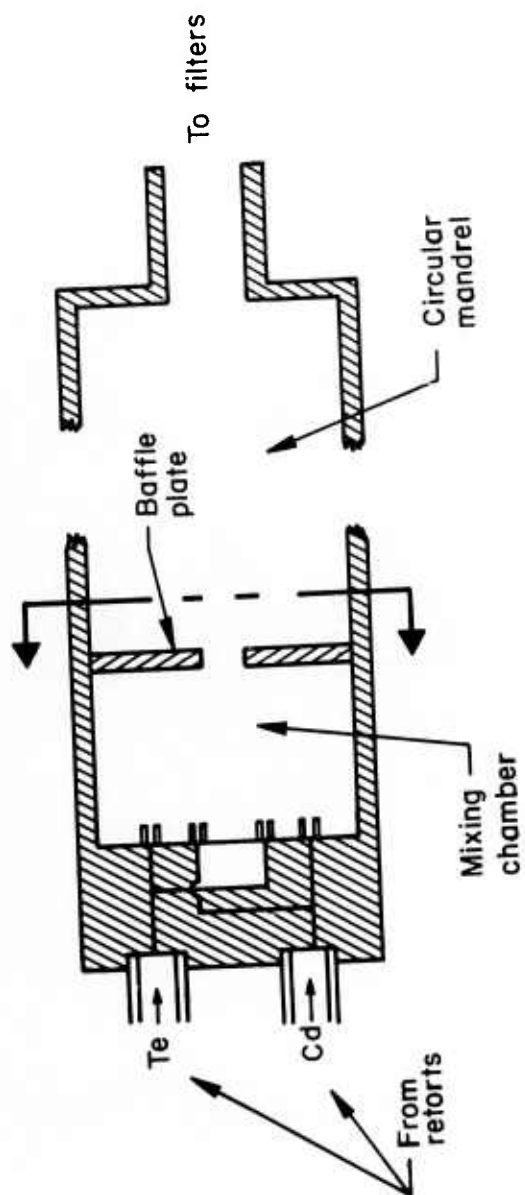


Figure 10. Initial Deposition Setup With Circular Mandrel

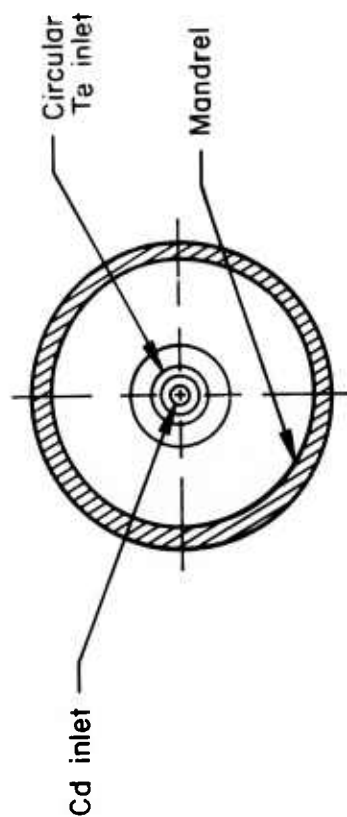
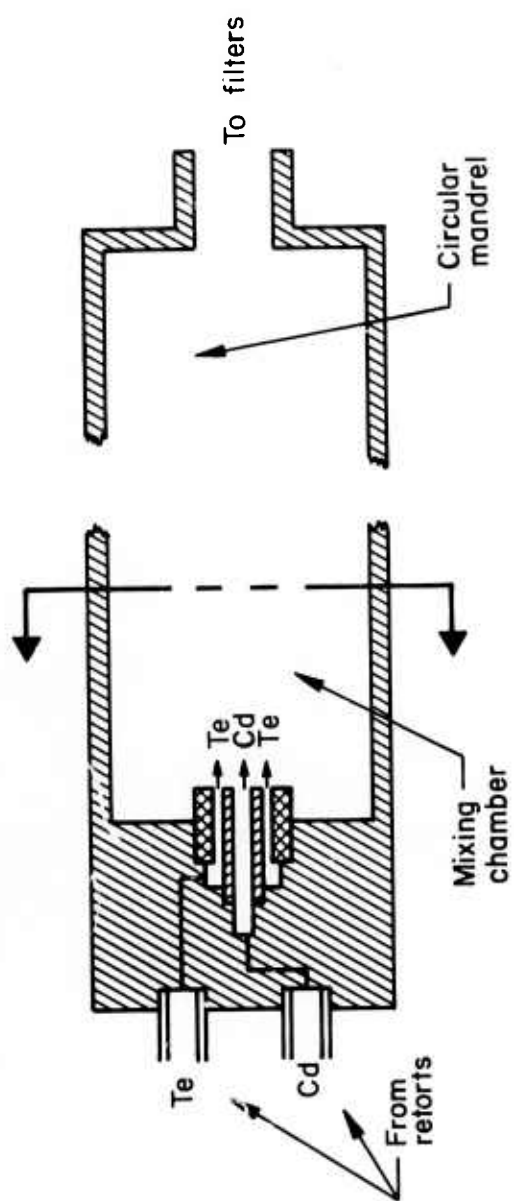


Figure 11. Deposition Chamber with Concentric Reactant Inlets

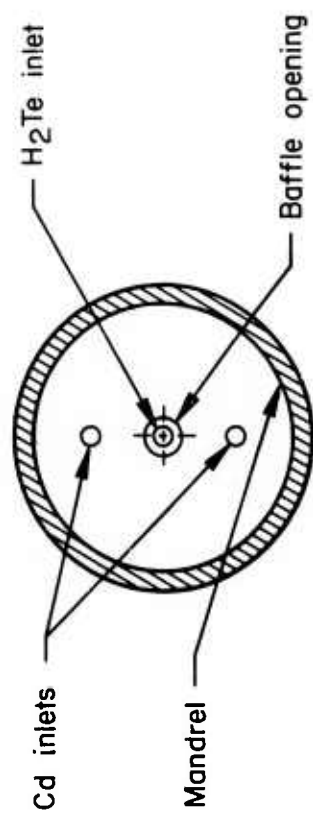
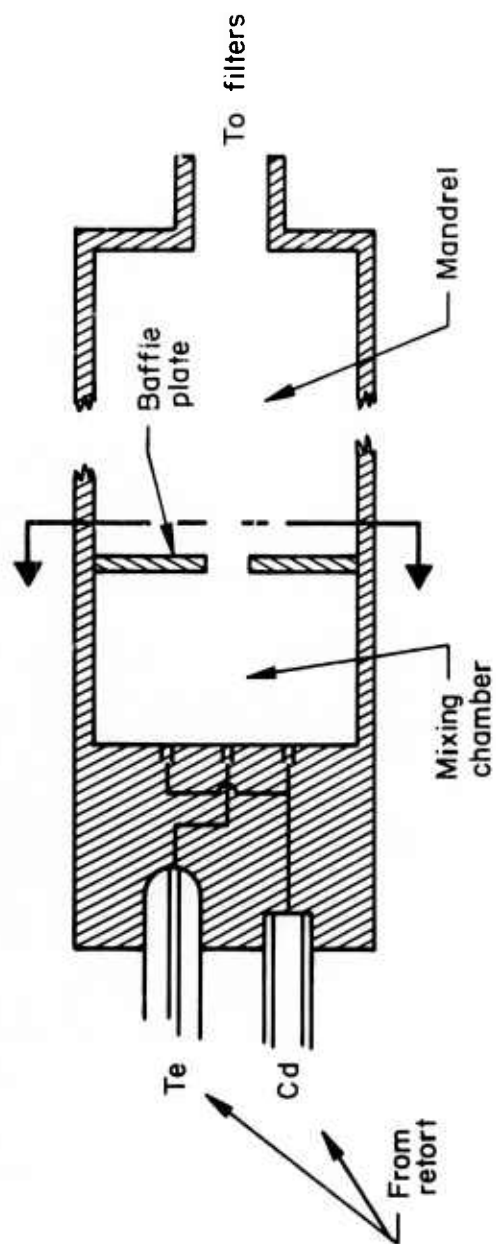


Figure 12. Mandrel Configuration Used With H₂Te and Dimethyl Tellurium

The design changes shown in Figures 13 and 14 were used in runs 36 thru 41. It was hoped the new configuration would force the flow of the reactants to the mandrel walls thereby producing a fairly uniform deposit. This was not the case, however, as CdTe was deposited at random in the mixing chamber or mandrel area.

Figure 15 shows a mandrel design which was quite different from the preceding ones in that the mandrel was placed perpendicular to the flow of the reactants. This basic design was used on three series of runs: Runs CdTe-42 thru -48, CdTe-49 thru -52, and CdTe-53 thru -61. In the first two series of runs Cd vapor was used as one reactant, with Te vapor and H_2Te as the other reactant in runs 42 through 48 and 49 thru 52 respectively. In both cases a fairly even deposition profile was attained on the vertical mandrel. In the last series of runs (53 thru -61) using this specific mandrel design, changes were made in the position and size of the reactant inlet holes in an attempt to improve the deposition profile.

Many of the design changes mentioned above, as well as those yet to be listed were made with the intention of improving the deposition profile throughout the mandrel area. It was also hoped that the proper mandrel design might help to eliminate physical voids which were formed as the CdTe was being deposited (see Experimental Section for information on void formation).

In runs CdTe-62 through -73 a venturi-type mixing chamber was used in conjunction with a vertical mandrel. Figure 16 shows this design. Temperature and pressure variations, as well as changes in mandrel position etc., were made during this series of runs. Polycrystalline CdTe of uniform thickness was deposited in a number of runs in this series. The material did still contain physical voids or cavities as mentioned previously.

Figure 17 shows the type of mandrel design used in the last series of runs (CdTe-74 through -100). In some of the runs (CdTe-74 thru -85)

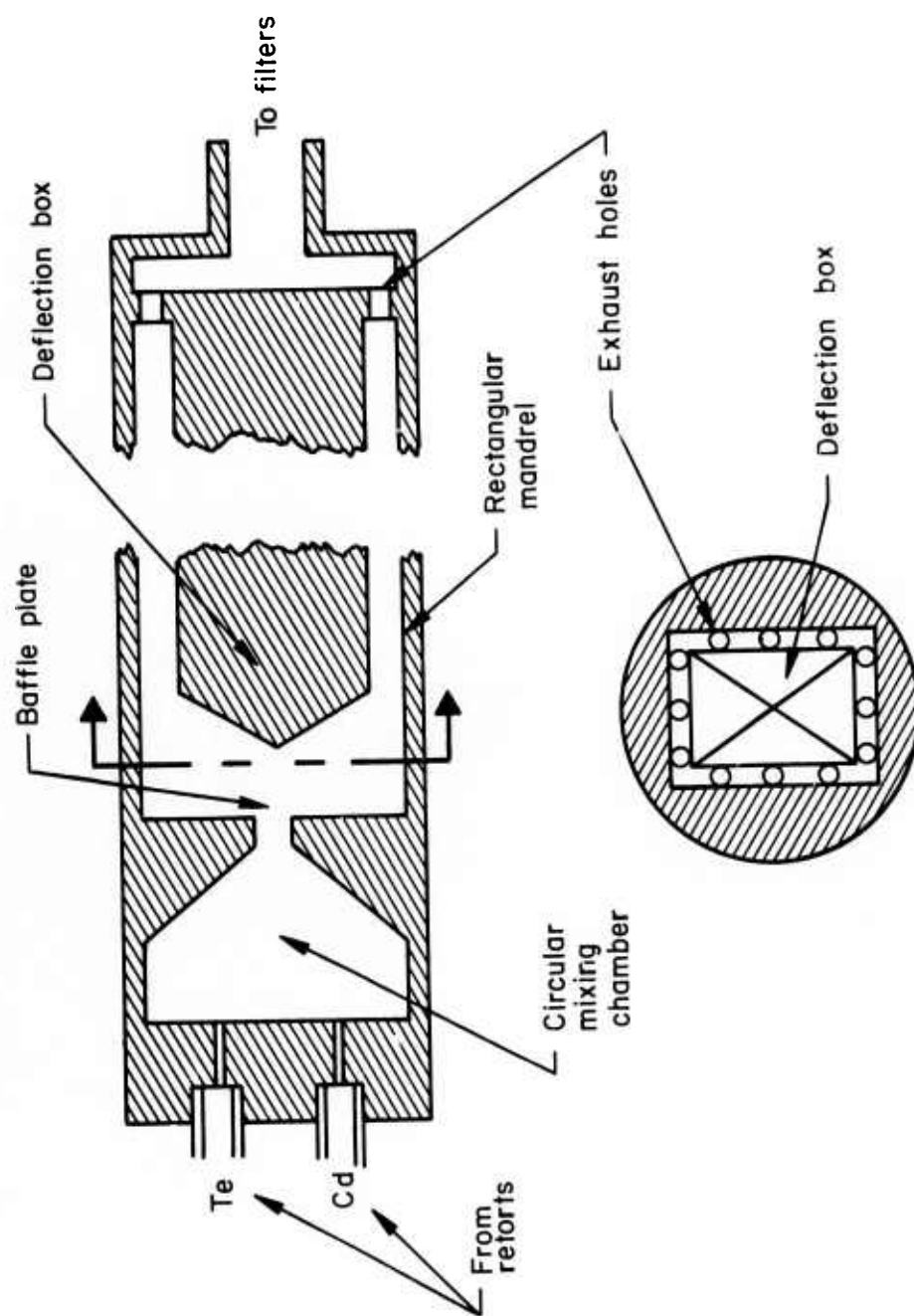


Figure 13. Mandrel Design Incorporating a Circular Mixing Chamber and a Deflection Plate in the Mandrel Area

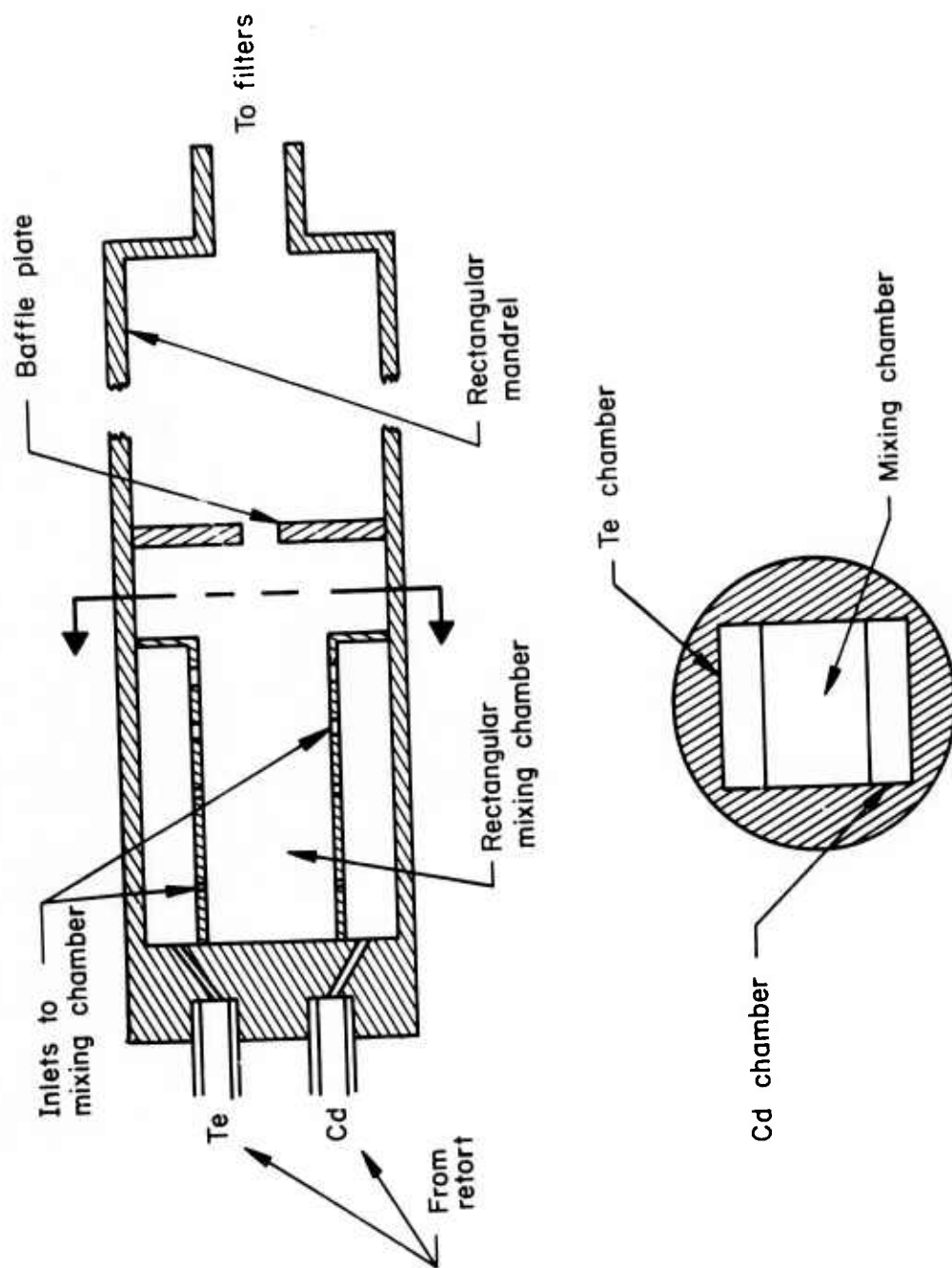


Figure 14. Set-up With Reactant Inlets Perpendicular to the Normal Flow

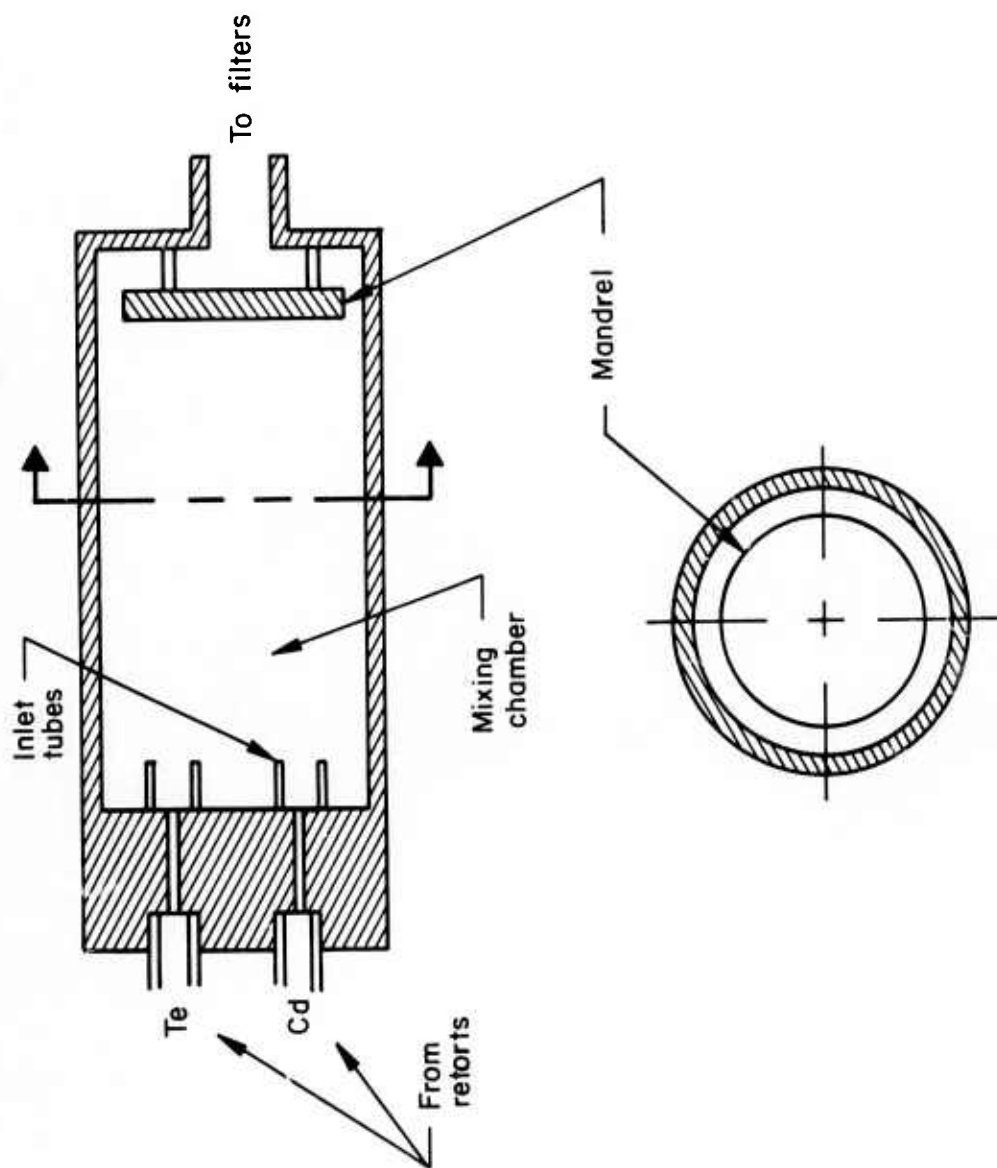


Figure 15. Deposition Set-up With Mandrel Perpendicular to Gas Flows

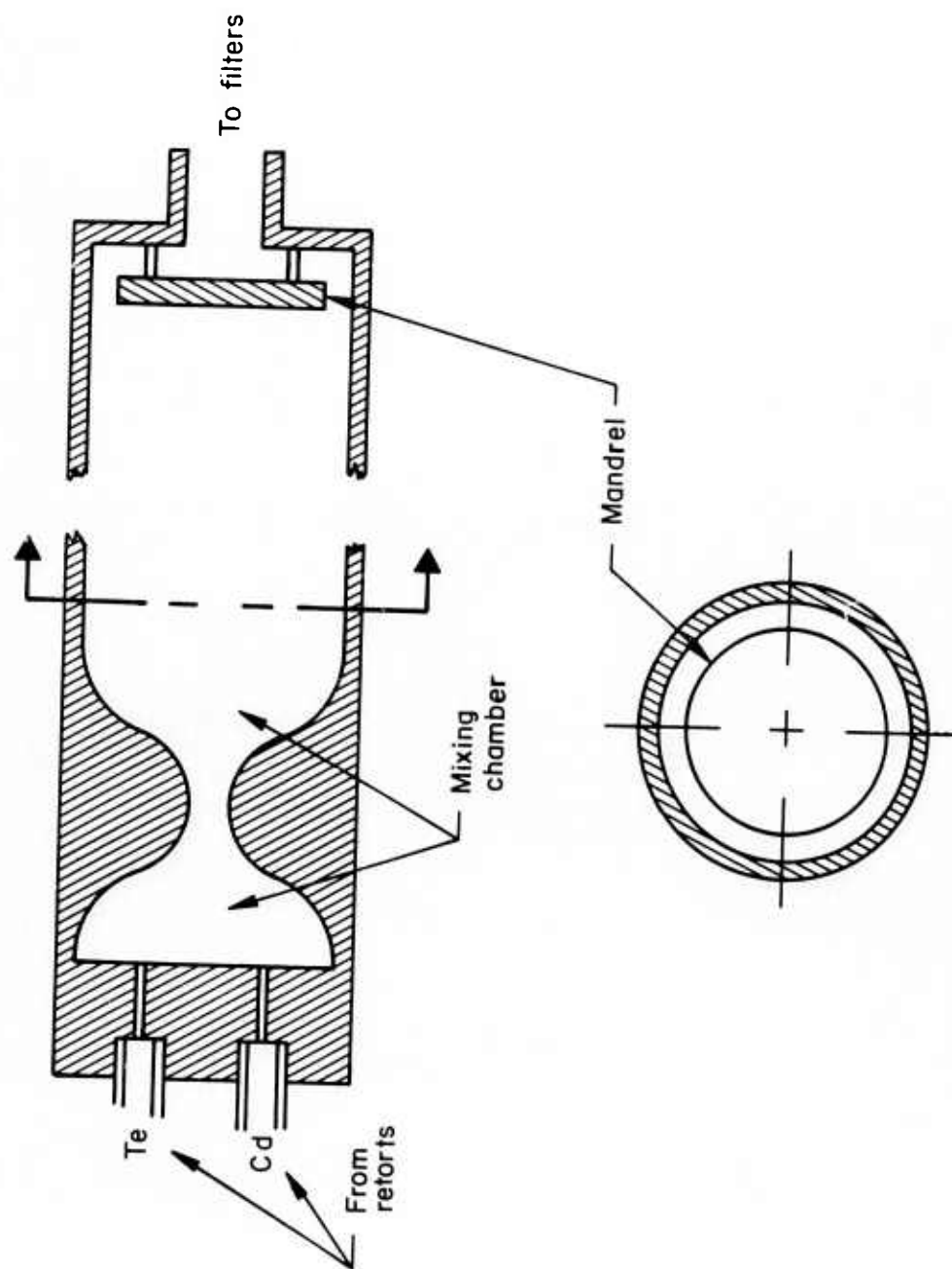


Figure 16. Design Using a Venturi-Type Mixing Chamber and a Vertical Mandrel

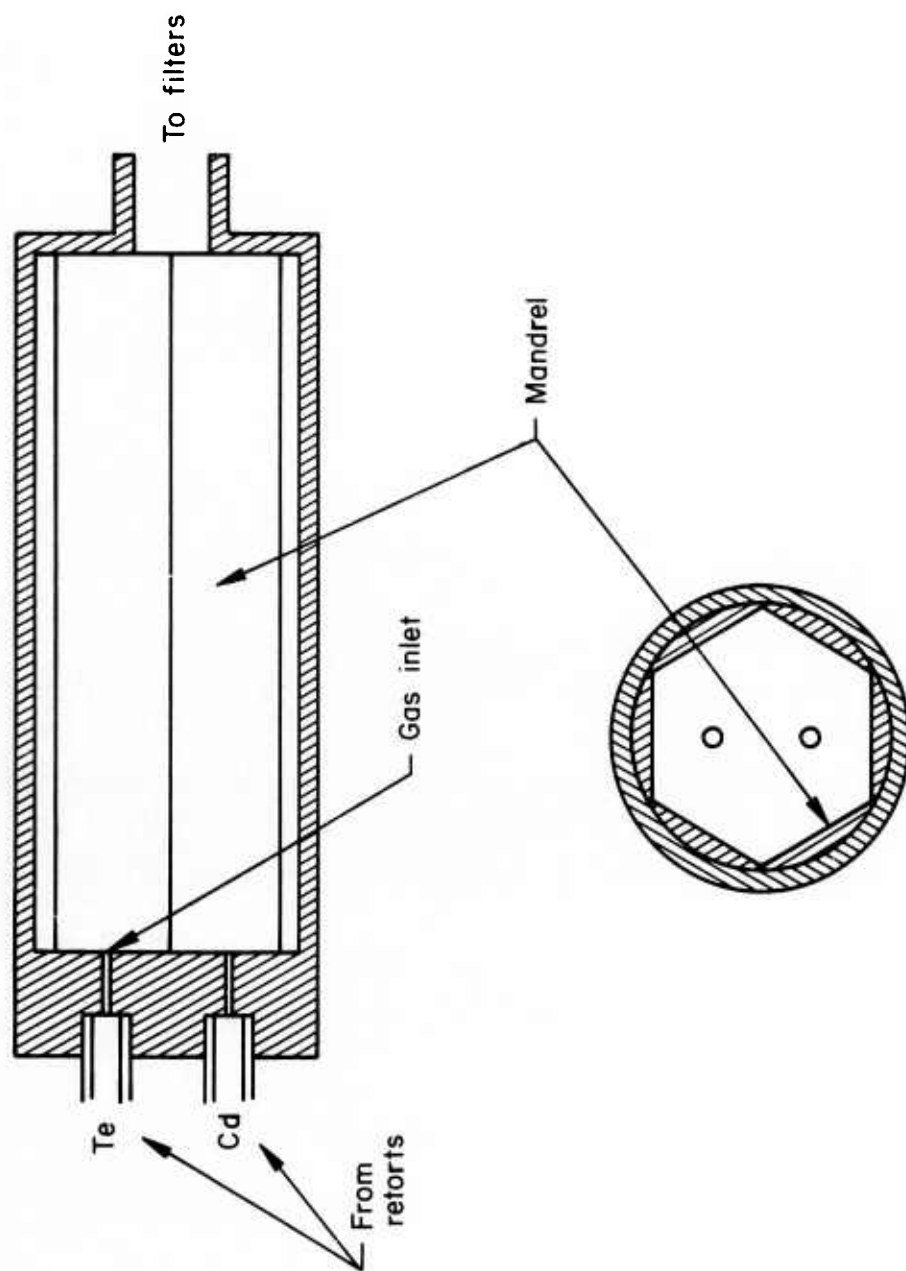


Figure 17. Design Using a Six-Sided Mandrel

this mandrel was used in conjunction with the venturi-like mixing chamber shown in Figure 16. By using the six-sided mandrel with the correct deposition temperature, pressure, and gas flows, it was possible to deposit CdTe in a fairly uniform manner over the entire surface of the mandrel. Again, cavities were present in most of the CdTe deposited using this setup.

The deposition characteristics of CdTe seem to be somewhat different than other II-VI compounds such as ZnSe or ZnS. The latter two compounds seem to prefer to react at the hot mandrel wall and to subsequently deposit there. Ideally, a CVD reaction should take place in this manner. In the CdTe reaction, however, material seems to prefer to form in the gas phase or to deposit on a mandrel which is perpendicular to the reactant flow. Successful deposits were finally made on a mandrel which was parallel to the reactant flows, however. It is difficult to say whether these differences in deposition behavior are due to kinetic or thermodynamic considerations in the various II-VI compounds.

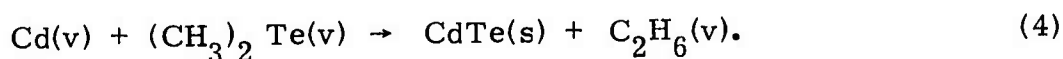
4. CVD of CdTe using metal-organics

a. Introduction

Originally, four possible reactions using organo-metallic Cd and Te compounds were proposed. These compounds are liquids with substantial vapor pressures at room temperature, so it was hoped that CdTe could be deposited at $\sim 300^\circ \text{C}$. This low deposition temperature would help to keep the native defect concentration in the material fairly low.

b. Experimental

Cadmium metal vapor and dimethyl tellurium were used in attempting to produce CVD CdTe using the reaction:



The basic furnace setup contained one retort (for molten cadmium) and a nozzle to feed the dimethyl tellurium into the mixing chamber. Figure 12 shows the mixing chamber and mandrel design.

Seven process runs (CdTe-17 through -23) were made to evaluate the above method of producing CdTe. The runs were carried out under a variety of temperatures and pressures (Table I). Cadmium telluride powder was produced in the first six runs. In the last run (CdTe-23), small crystals of CdTe were formed, but they did not form a coherent layer of material.

The dimethyl tellurium did not offer any advantages as a Te source. It decomposes at $\sim 300^\circ \text{C}$, so essentially Te and Cd vapors were reacting to form the CdTe powder. After judging the results of using dimethyl tellurium as one of the starting material, it was decided not to pursue the use of organo-metallic reactants any further. They are quite costly ($\sim \$4.00/\text{gm}$), highly toxic, and they did not seem to offer the optimum route by which to deposit CVD CdTe.

5. CVD of CdTe using elemental Cd and Te

a. Introduction

This method is certainly the most straight-forward and economical way of producing CdTe. By going directly from the elements to polycrystalline CdTe, there is not the added expense of preparing an intermediate compound such as a metal-organic or hydrogen telluride gas.

b. Experimental

Cadmium and tellurium metal vapors were combined to produce CVD CdTe according to reaction (5):



$$\Delta G^\circ_f, 700^\circ \text{C} = -20.5 \text{ Kcal/mole}$$

$$\Delta G_{\text{RX}} = -4.4 \text{ Kcal/mole}$$

TABLE I
DEPOSITION CONDITIONS OF EXPERIMENTAL CdTe RUNS

Run No.	Mandrel Temp (° C)	Furnace Pressure (torr)	Cd Retort Temp (° C)	Te Retort Temp (° C)	Gas over Cd (lpm)	Gas over Te (lpm)	Dep Time (hrs)	Cd(v) Te(v) Ratio	Mandrel & Mixing Chamber Design
1	660	50	565	660	H ₂ 0.7	H ₂ 0.7	2	---	Fig. 10
2	785	700	490	610	Ar 0.3	Ar 0.3	2	---	Fig. 11
3	820	650	575	690	0.6	0.6	2	1.0	
4	720	630	575	650	0.6	0.6	2	1.2	
5	715	650	575	650	H ₂ 0.77	H ₂ 0.77	2	2.5	
6	720	200	550	630	0.77	0.77	2	5.5	broken retort no deposition
7	710	31	480	560	0.57	0.57	2	1.4	
8	700	19	485	570	0.2	0.2	2	1.4	
9	695	9	490	565	0.6	0.6	2	broken retort	
10	705	5	490	565	0.6	0.6	2	no deposition	Fig. 11
11	720	10	520	575	0.6	0.10	1.5	1.2	Fig. 10
12	705	8	520	575	0.6	0.24	4	1.7	
13	Abort	---	---	---	---	---	---	---	
14	635	10	501	550	0.22	0.22	3	2.7	
15	815	10	480	550	0.4	0.37	2	1.4	Fig. 10
16	730	11	470	530	0.7	0.7	3.5	0.7	

Table I (Cont'd)

Run No.	Mandrel Temp (° C)	Furnace Pressure (torr)	Cd Retort Temp (° C)	Te Retort Temp (° C)	Gas over Cd (lpm)	Gas over Te (lpm)	Dep Time (hrs)	Cd(v) Te(v) Ratio	Mandrel & Mixing Chamber Design
					<u>N₂</u>	<u>N₂</u>			
17	580	600	545	---	1.0	1.0	2	no Te pickup	Fig. 12
18	740	700	580	---	0.8	1.0	2	13.5	
19	780	100	515	---	1.0	1.4	2.5	14.0	
20	710	91	460	---	0.9	2.4	4	0.35	
21	745	82	490	---	0.9	2.4	2	0.45	
22	720	86	440	---	0.9	2.4	2	1.6	
23	830	90	555	---	0.9	2.4	3	4.0	
24	Aborted								Fig. 10
25	840	9.5	490	560	0.8	0.8	2	1.4	
26	840	6.0	470	560	0.6	0.6	3	1.2	
27	810	4.0	450	530	0.4	0.4	3	0.6	
28	740	5.0	430	510	0.4	0.4	3.5	0.6	
29	800	8.0	440	530	0.8	0.8	4	1.0	
30	760	7.0	425	515	0.8	0.8	4	1.6	

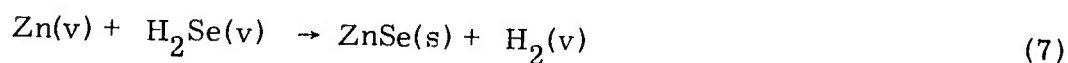
Table I (Cont'd)

Run No.	Mandrel Temp (°C)	Furnace Pressure (torr)	Cd Retort Temp (°C)	Te Retort Temp (°C)	Gas over Cd (lpm)	Gas over Te (lpm)	H ₂ Te (moles/hr)	Gas with H ₂ Te (lpm)	Dep Time (hrs)	Cd(v) Te(v) Ratio	Mandrel & Mixing Chamber Design
31	730	10.0	405	---	0.8	---	---	0.6	3	---	Fig. 12
32	760	9.0	410	---	0.8	---	0.03	0.6	3	---	
33	760	9.0	390	---	0.8	---	0.05	0.6	3	2.0	
34	700	10.0	400	---	0.8	---	0.05	0.6	-	0.6	
35	750	11.0	420	---	0.8	---	0.05	0.6	2	1.0	
36	730	13.0	420	530	0.8	0.8	---	---	2.5	1.0	Fig. 13 and Fig. 14
37	740	10.0	430	540	0.8	0.8	---	---	5	1.0	
38	810	20.0	430	550	0.4	0.4	---	---	2.5	0.3	
39	770	5.0	420	540	0.4	0.4	---	---	3	0.6	
40	740	20.0	400	510	0.8	0.4	---	---	3.5	2.0	
41	720	10.0	410	580	0.8	0.8	---	---	4	1.5	
42	720	10.0	460	590	0.8	0.8	---	---	4	1.2	Fig. 15
43	690	15.0	420	510	0.8	0.8	---	---	3	1.2	
44	690	15.0	390	590	0.8	0.8	---	---	5	1.3	
45	690	12.0	335	540	0.8	0.8	---	---	6	1.0	
46	Abort										
47	690	15.0	420	560	0.4	0.4	---	---	5	---	Fig. 15
48	720	14.0	315	490	0.4	0.4	---	---	6	0.5	
49	Abort										
50	650	10.0	340	---	0.8	---	0.2	0.6	1	0.2	
51	650	10.0	350	---	0.8	---	0.2	0.6	5	2.0	
52	690	15.0	310	---	0.8	---	0.1	0.6	4.5	4.0	
53	710	14.0	320	480	0.6	0.6	---	---	6	0.1	
54	710	16.0	340	500	0.6	0.6	---	---	6	0.1	
55	Abort										
56	720	20.0	36.0	530	0.6	0.6	---	---	20	---	
57	710	10.0	330	510	0.6	0.6	---	---	12	0.6	
58	710	27.0	370	525	0.6	0.6	---	---	12	---	
59	710	42.0	370	520	0.6	0.6	---	---	20	0.4	
60	620	21.0	380	530	0.6	0.6	---	---	4.5	0.6	
61	750	21.0	360	530	0.6	0.6	---	---	3.5	0.6	
62	720	20.0	416	530	0.5	0.5	No Te pickup		3.5	---	
63	750	18.0	415	520	0.5	0.5	---	---	5.0	1.0	
64	750	6.0	420	520	0.5	0.5	---	---	4.5	1.0	
65	745	12.0	430	540	0.5	0.5	---	---	3.0	1.3	Fig. 16

Table I (Cont'd)

Run No.	Mandrel Temp (° C)	Furnace Pressure (torr)	Cd Retort Temp (° C)	Te Retort Temp (° C)	Gas over Cd (lpm)	Gas over Te (lpm)	H ₂ Te (moles/hr)	Gas with H ₂ Te (lpm)	Dep Time (hrs)	Cd(v) Te(v) Ratio	Mandrel & Mixing Chamber Design
66	770	20.0	420	535	0.5	0.5	New set-up	---	3.5	1.2	Fig. 16
67	780	18.0	430	545	0.5	0.5	---	---	4.0	1.1	
68	850	22.0	420	550	0.5	0.5	---	---	3.0	0.7	
69	Abort										Fig. 17
70	840	16.0	420	---	0.5	---	0.1	0.5	2.5	~4.3	
71	860	20.0	450	---	0.5	---	0.1	0.5	3.8	4.0	
72	720	14.0	315	525	0.5	0.5	---	---	9.0	0.05	Fig. 17
73	Abort										
74	790	15.0	350	540	0.5	0.5	---	---	9.0	0.3	
75	810	16.0	340	550	0.5	0.5	---	---	8.0	0.35	Fig. 17
76	850	16.0	380	550	0.5	0.5	---	---	4.0	0.6	
77	840	20.0	380	550	1.0	0.75	---	---	4.0	0.1	
78	840	13.0	410	---	0.5	---	---	0.5	4.5		Fig. 17
79											
80	790	16.0	390	---	0.5	---	0.3	0.5	4.5	0.6	
81	790	10.0	390	---	0.5	---	0.2	0.5	5.5	1.9	Fig. 17
82	790	20.0	380	---	0.5	---	0.3	0.5	3.8	0.9	
83	780	10.0	390	---	H ₂	0.5	---	0.5	5.0		
84	790	10.0	400	---	H ₂	0.5	0.66	0.5	5.0	0.7	Fig. 17
85	730	12.0	390	---	H ₂	0.5	0.25	0.5	7.0	1.8	
86	730	6.0	415	570	N ₂	0.5	---	---	~3.0	~0.5	
87	730	15.0	430	590	0.5	0.5	---	---	~7.0	~1.0	Fig. 17
88	Abort										
89	720	15.0	340	470	0.5	0.5	---	---	~7.0	~0.5	
90	720	17.0	290	470	1.5	1.5	---	---	~4.0	~0.5	Fig. 17
91	720	17.0	320	450	H ₂	1.5	---	---	~6.0	~1.0	
92	750	20.0	330	440	H ₂	1.5	---	---	5.0	1.0	
93	640	20.0	330	430	0.5	0.5	---	---	6.5	1.5	Fig. 17
94	640	10.0	340	---	0.5	0.5	---	---	3.0	0.3	
95	620	20.0	350	460	0.5	0.5	0.19	0.5	6.5	1.1	
96	600	16.0	340	---	0.5	0.5	---	0.5	5.5	0.75	Fig. 17
97	580	20.0	350	450	0.5	0.5	0.08	---	8.0	1.2	
98	620	20.0	360	460	H ₂	0.5	---	---	30.0	1.9	
99	650	20.0	360	---	0.5	---	---	0.042	22.0	1.0	Fig. 17
100	640	20.0	370	---	0.5	---	~0.06	0.5	30.0	~1.5	

When depositing ZnSe according to the following reaction:



$$\Delta G^\circ_{f, 700^\circ \text{C}} = -37.8 \text{ Kcal/mole}$$

$$\Delta G_{\text{RX}} = -26.3 \text{ Kcal/mole}$$

the free energy values for equivalent deposition conditions are somewhat more negative for ZnSe than for CdTe. It was felt, however, that given the free energy conditions above, it should be possible to deposit CdTe by CVD techniques.

Of the one-hundred (100) deposition runs made under this contract, the majority were made utilizing reaction (5). The basic furnace setup always contained two retorts (one for molten Cd and one for molten Te) as shown in Figure 9, but of course the mandrel and mixing chamber designs were varied as discussed in Sec. II. D. 3. Deposition parameters such as pressure, temperature, and molar input were varied from run to run as is shown in Table I.

c. Results

Approximately seventy experimental runs were made using the two elements as reactants. As one can see from Table I, both hydrogen and nitrogen were used as carrier gases in various runs. Rather than taking time to describe all of the runs a few of the more significant runs will be discussed.

A coherent deposit of polycrystalline material was formed for the first time in run CdTe-15. A small amount (0.5 x 0.5 x 0.030 in.) of theoretically dense CdTe was formed. The run was carried out at 815° C with a Cd(v)/ Te(v) ratio of 1.4. The resistivity of the material was $\sim 5 \times 10^5$ ohm-cm. An in-line transmittance curve for the as-deposited CdTe is shown in Figure 18.

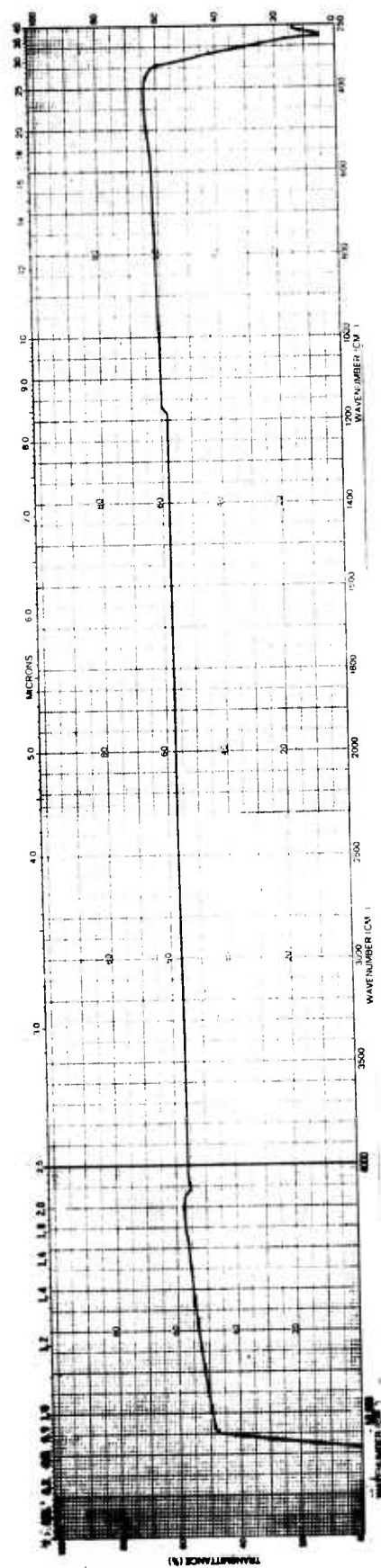


Figure 18. In-Line Transmittance of Run CdTe-15

The fact that the curve remained quite flat with a sharp break at $\sim 30 \mu\text{m}$ indicated that the free carrier concentration of the material was fairly low.

Up to run CdTe-42, the runs were successful in that small pieces of polycrystalline CdTe were deposited (mandrel temperature 700°C to 850°C) randomly in the mandrel area; however, no uniform thickness profile throughout the mandrel area could be attained. Pores from $100 \mu\text{m}$ to $300 \mu\text{m}$ were present in the material along grain boundaries. Typical IR transmission from 2.5 to $35 \mu\text{m}$ was $\sim 50\%$.

After run CdTe-42 the deposition chamber design of the furnace was changed to that shown in Figure 9. The two elements were allowed to mix in an open chamber and then flow around a mandrel ~ 4 in. downstream. The temperature in the mixing zone was somewhat higher than that in the mandrel area as is shown in Figure 19. The reactants essentially became supersaturated at the lower mandrel temperature. This made it possible for the polycrystalline CdTe to form a coherent deposit on the mandrel plate. The deposits were 2×2 in., and up to 200 mils thick.

The CdTe deposited in this manner also contained voids or pores along the grain boundaries. The first 20 mils of material was quite pore-free, but subsequently the CdTe seemed to grow on certain crystal faces preferentially, thus forming voids at the grain boundaries. Figure 20 shows an in-line transmittance curve from run CdTe-54. This material was ~ 20 mils thick and somewhat pore-free. The transmittance is 64% at $10 \mu\text{m}$. The theoretical transmission value is $\sim 66\%$.

The in-line transmittance curve for a thicker (~ 0.10 in.) deposit of CdTe is shown in Figure 21. Both curves break quite sharply in the multiphonon band region at $\sim 35 \mu\text{m}$. This indicates that the number of free carriers in the CdTe is quite low. Since free carrier absorption depends on wavelength approximately as λ^3 in this spectral range, the percent transmittance would tail off gradually as the wavelength increased if a large number of free carriers were present.

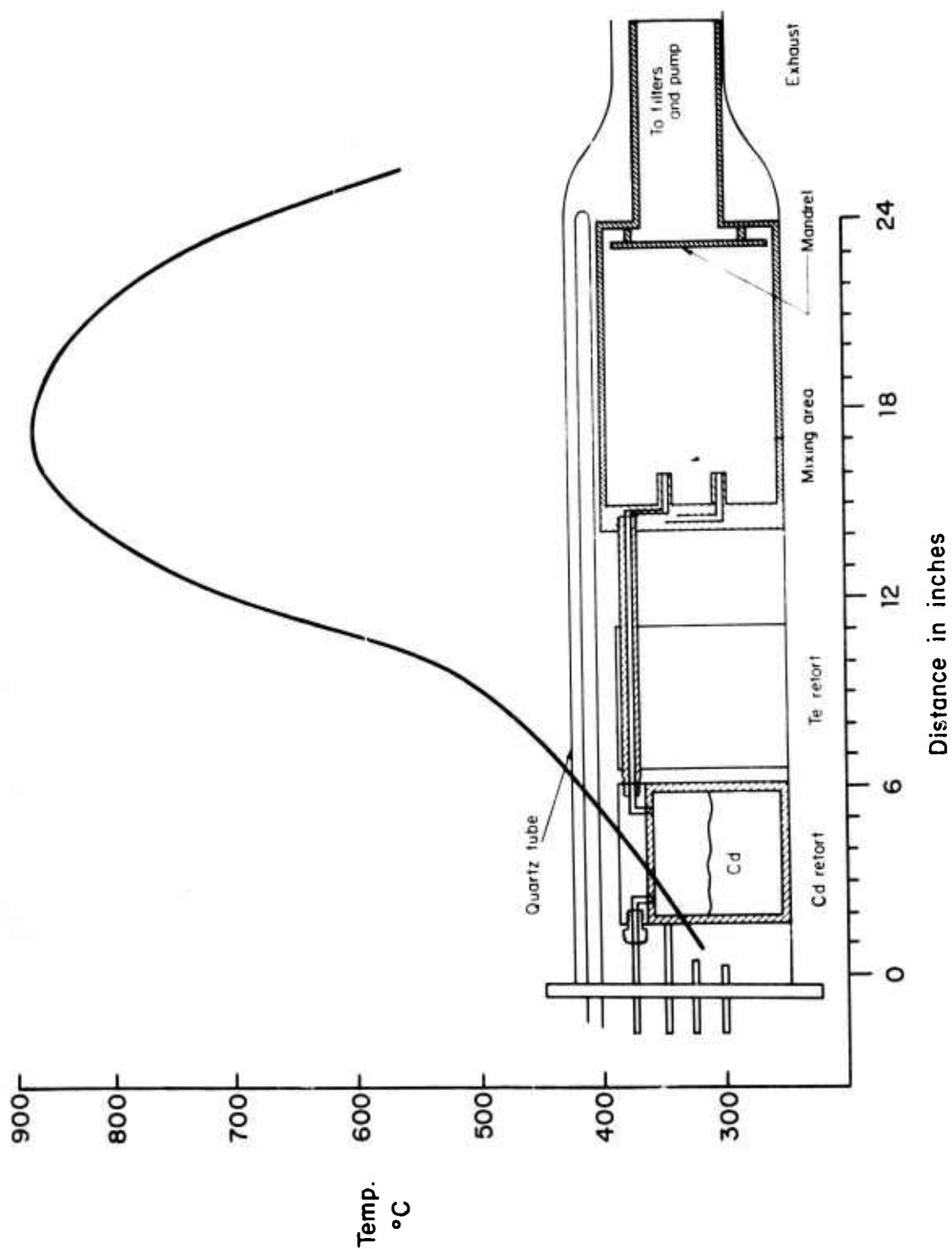


Figure 19. Temperature Profile of Furnace Used to Allow Supersaturation of the Reactants to Occur in the Mandrel Area

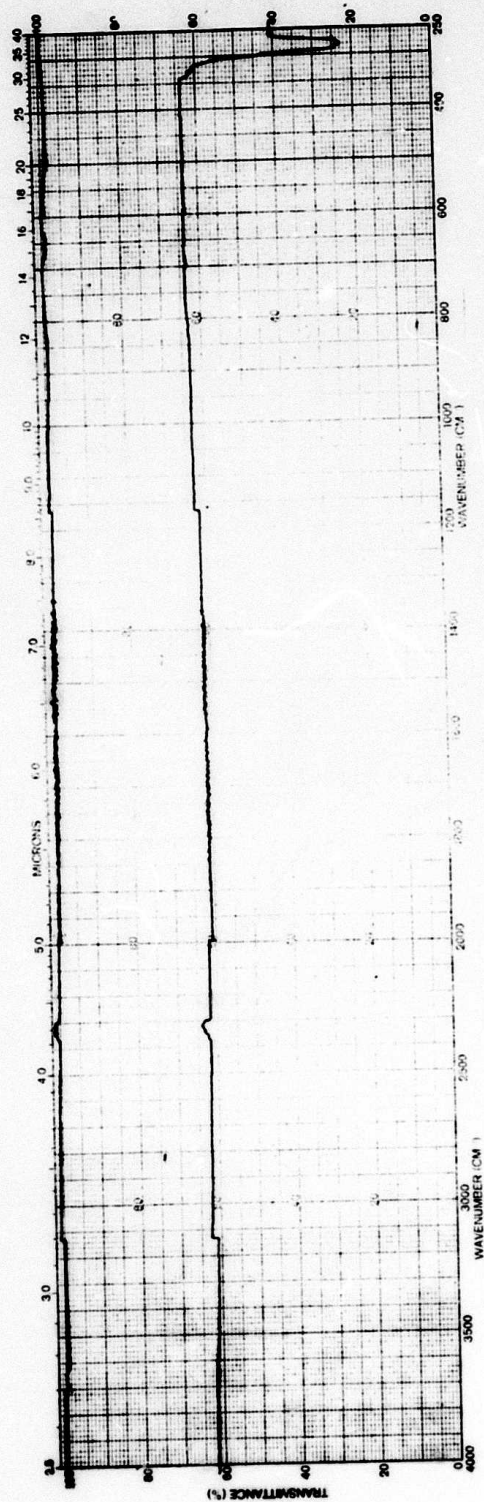


Figure 20. In-Line Transmission of CdTe-54, Thickness = 0.020 in.

Reproduced from
best available copy.

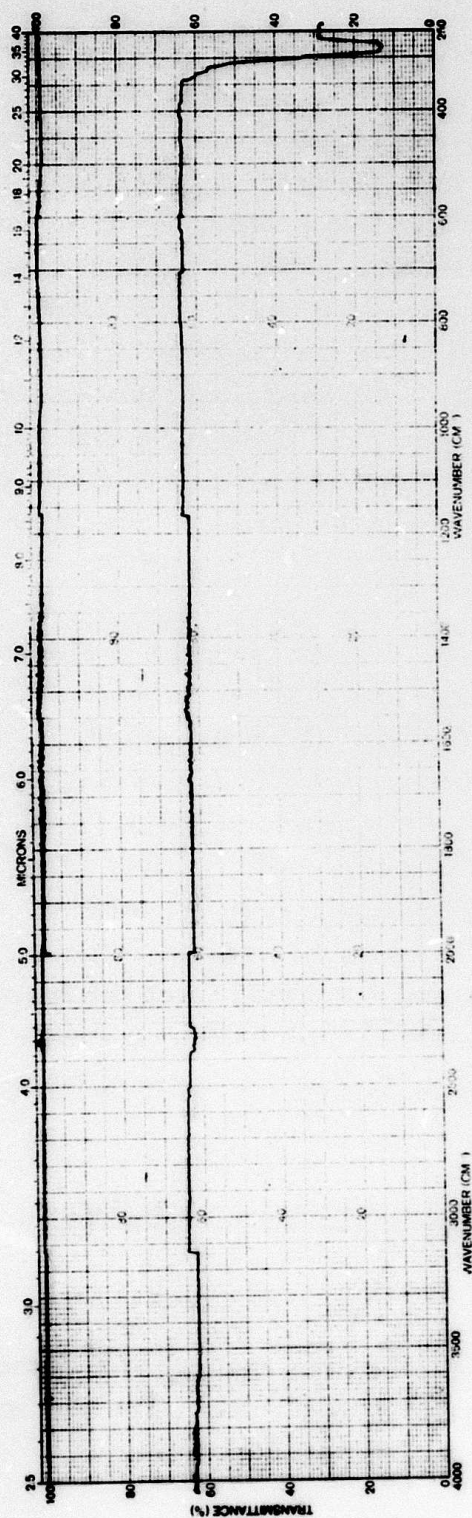


Figure 21. In-Line Transmission of CdTe-58, Thickness = 0.100 in.

As mentioned earlier, it was felt that voids or pores were present in the polycrystalline CdTe because some grains or crystal faces grow faster than others. From the free energies of reaction shown earlier in Section II. D. 5. b it is evident that ΔG_{RX} for CdTe under the conditions which we employ turns out to be more positive than -5 Kcal/ mole. If we compare that value with the ΔG_{RX} for the formation of polycrystalline ZnSe, we see that ZnSe forms with a driving force of -26.3 Kcal/ mole. Other II-VI compounds such as ZnS also deposit with a driving force of -20 to -30 Kcal/ mole. Based on this experience, the CdTe deposition conditions were changed to make the ΔG_{RX} for CdTe more negative. It was hoped that with this larger driving force present, the individual Cd and Te atoms would not deposit preferentially on certain grains, and thus the formation of pores or voids would be reduced or eliminated.

In accordance with the above idea, the normal deposition temperature was lowered from $\sim 730^\circ \text{C}$ to $\sim 600^\circ \text{C}$ in the last series (CdTe-93 through CdTe-98) of elemental CdTe runs. If concentrations and pressure were kept constant this drop in temperature would decrease the free energy of reaction for equation (5) from -4.4 Kcal/ mole at 700°C to -11.7 Kcal/ mole at 600°C . This theory may have some validity. Run CdTe-97 was deposited at 580°C (Table I), and upon examination it seemed to contain a minimum of voids and cavities. The deposited material within the mandrel consisted of small uniform grains rather than the uneven pattern of small and large crystallites present in material deposited at a higher temperature. Because of the thinness of the deposit, further evaluation of this run was not possible.

6. CVD of CdTe using elemental Cd and H_2Te gas

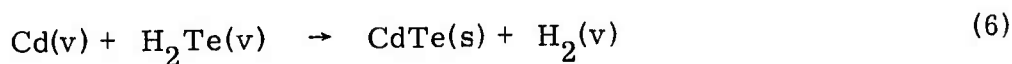
a. Introduction

This method for producing CdTe is an analog of the method which has been so successful in depositing zinc selenide. The hydrogen

telluride gas (H_2Te) is much more unstable and thus much more difficult to manufacture than hydrogen selenide. Thus the main drawback in this method lies in the cost of the gas.

b. Experimental

Cadmium vapors and H_2Te gas were combined to produce polycrystalline CdTe according to reaction (6):



$$\Delta G^\circ_{F, 700^\circ \text{C}} = -20.5 \text{ Kcal/mole}$$

$$\Delta G_{\text{RX}} = -2.8 \text{ Kcal/mole}$$

The free energy for the above reaction is essentially the same at 700°C as that for producing CdTe from the elements via reaction (5).

During the course of this contract twenty (20) runs were made employing H_2Te as the tellurium source. The timing of the runs depended on the availability of the gas from the supplier. The mixing chamber and mandrel setups used to deposit the CdTe have been shown previously in Figures 15, 16, and 17. Deposition parameters such as temperature, pressure, and molar input ratio for the various runs are listed in Table I.

c. Results

The results obtained on the majority of the CdTe runs made using H_2Te gas were essentially the same as the results obtained when using Te vapor as one of the reactants. Polycrystalline CdTe was formed at mandrel temperatures from 700° to 800°C . The thickness profile throughout the mandrel area was more uniform than with comparable runs made with elemental Te vapors as the Te source. In-line transmittance of the as-deposited material ranged from 50 to 60 percent between 2.5 and $35 \mu\text{m}$.

Physical voids or cavities were also present in the CdTe. A picture of these voids as viewed through an IR microscope at 100X is shown in Figure 22. The largest voids are up to 30 μm in size.

In the last series of runs (CdTe-94, -96, -99, -100) the deposition temperature was lowered by $\sim 100^\circ\text{C}$ from previous runs in order to obtain a more negative ΔG_{RX} for the deposition process. As explained in Sec. II.D.5.c. it was felt that the larger driving force might eliminate the growth of preferential crystal faces believed to be responsible for the void formation.

Run CdTe-100 seemed to be quite successful in this respect. When viewed through the IR microscope no voids were seen in a polished CdTe specimen (100X). This was in marked contrast to the material from run CdTe-71 shown previously in Figure 22. An in-line transmittance curve from the visible to 40 μm is shown in Figure 23. The transmission at 10 μm is close to the theoretical value of 66 percent. The flatness of the curve again indicates the absence of a large number of free carriers. Run CdTe-100 obviously produced the best polycrystalline CdTe made under this contract.

E. Physical Data

The primary goal of this research was to develop a suitable method or methods to chemical vapor deposit polycrystalline CdTe. Many of the runs were of short duration, and much of the material contained voids and cavities which we were trying to eliminate by changing the various deposition parameters. As a result a large amount of time was not expended on collecting physical data.

Some typical properties of CVD CdTe are shown in Table II. This data was gathered from specimens taken from six of the 100 runs made, and the listed values are averages of several samples. The best in-line transmittance ($\sim 66\%$ at 10 μm) and electrical resistivity (2.0×10^7 ohm-cm) were measured on specimens from run CdTe-100.

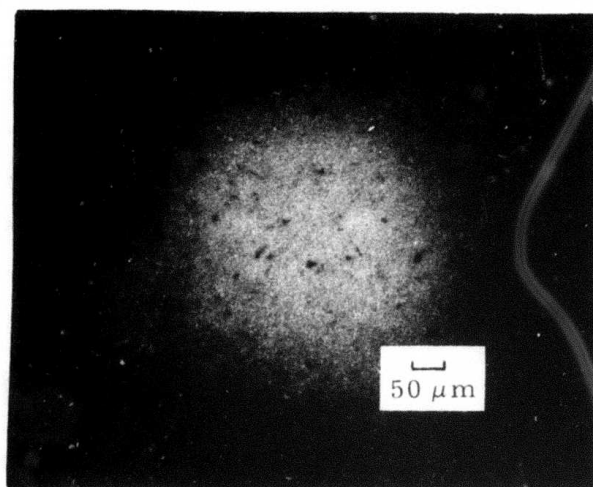


Figure 22. Voids in As-Deposited Polycrystalline Cadmium Telluride, Run CdTe-71 (100X)

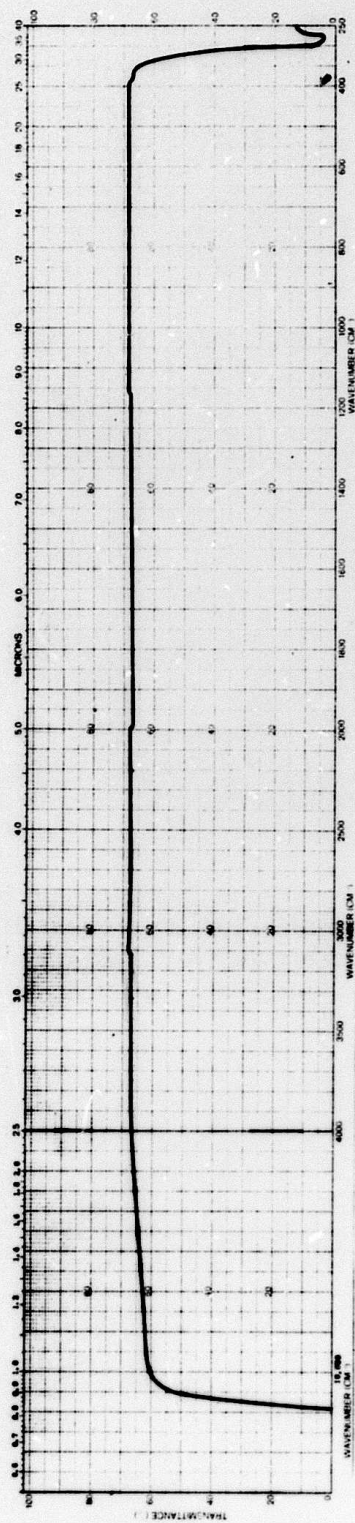


Figure 23. In-Line Transmittance from the Visible to 40 μm
Run CdTe-100

The absorption coefficient on a few thin CdTe specimens (~ 10 mils) was measured by laser calorimetry. The values obtained were not taken as valid numbers since the surface losses on a thin specimen may overshadow the bulk losses resulting in an incorrect value for the absorption coefficient.

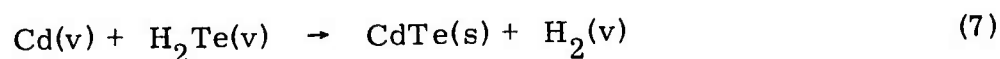
TABLE II

PHYSICAL PROPERTIES OF CVD CADMIUM TELLURIDE

As deposited material	P type
Knoop hardness (50 gm)	40
Grain size (μm)	350
Density at 25° C	5.83 gm/cm ³
Transmission limits	0.83 to 35 μm
Transmittance (1.0 to 25 μm)	64 to 66%
Thermal expansion (RT to 300° C, $\times 10^{-6}/^{\circ}\text{C}$)	4.94
Electrical resistivity (ohm-cm)	2.5×10^3 to 2.0×10^7

III. CONCLUSIONS

Polycrystalline cadmium telluride has been successfully deposited by chemical vapor deposition techniques. Two methods have been utilized to give polycrystalline CdTe deposits of theoretical density as shown by equations (5) and (7):



The main problem which was partially overcome in the latter stages of the program concerned the formation of physical voids or cavities in the material during deposition. It is felt that these voids are formed when certain crystal faces grow more rapidly than others. As these rapidly growing crystal faces meet they block the flow of reactants to the slower growing faces and cause the formation of cavities. The best conditions for the deposition of relatively void-free CdTe are the following:

	<u>Rx (5)</u>	<u>Rx (7)</u>
Deposition Temp	580° C	640° C
Deposition Pressure	20 torr	20 torr
Cd(v)/ Te(v) Molar Ratio	1.2	1.5

In the deposition of II-VI compounds such as CdTe and ZnSe, it appears that a driving force or free energy more negative than -10 Kcal/ mole is essential for a good crystalline deposit.

IV. FUTURE WORK

A. Introduction

Now that two basic CVD processes have been established for the deposition of polycrystalline CdTe, three methods can be used to improve the optical and mechanical properties of CVD cadmium telluride. The first technique involves looking at a wider range of deposition conditions (placing ΔG_{RX} for CdTe in the -10 through -25 Kcal/ mole range) and noting how the formation of voids is affected by changing the deposition parameters. The second and third techniques involve adding dopants to the CdTe during the deposition process. The effect of these additions on the physical properties of the CdTe would be noted.

B. Elimination of Internal Voids

The main problem associated with deposition of polycrystalline CdTe at this point centers around the formation of voids or cavities within the material.

Voids with well developed facets have been found in CdTe which has been grown by vapor transport methods.¹⁰ Facets have also been noted in epitaxially grown $Hg_{1-x}Cd_xTe$.¹¹ The authors concluded that in general a highly faceted surface was undesirable because the various faceted crystallites joint together to entrap voids or to form crystalline subboundaries. It is felt that voids or pores occur in the CVD CdTe due to faceting wherein some grains or crystal faces grow faster than others.

The free energy of reaction is determined by such parameters as the concentration of reactants, reaction pressure, and reaction temperature. A matrix of runs will be carried out involving the most promising of the two reactions mentioned previously. In this matrix, the above parameters will be varied systematically to determine the conditions for producing optimum material which will be free of voids.

C. Hardness and Strength Increase by Cation Additions

The hardness and strength of a relatively brittle polycrystalline material such as cadmium telluride or zinc selenide can be increased by reducing its grain size, adding ions to form a solid solution (both of similar and dissimilar valency), and by adding a second phase that is precipitated in situ or through subsequent heat treatments. In the case of ZnSe, experimental work has already been done on increasing strength by decreasing grain size. A 50 percent increase in hardness has been obtained (from ~ 100 to 150 Kg/mm^2). A further increase in strength and hardness has also been observed by substituting sulfur for selenium. In this case the hardness has been increased from 100 Kg/mm^2 to $\sim 250 \text{ Kg/mm}^2$ with a 10 mole percent substitution.

It is suggested by data in the literature on other systems that dramatic increases in hardness can be attained with aliovalent* additions. For example, in the NaCl system, hardness and yield strength have been increased by factors of 5 to 25 by additions of ions such as Cd^{+2} or Ba^{+2} at concentration levels of 200 to 2000 ppm. On the atomic scale several mechanisms have been postulated to explain the observed results. Although these mechanisms differ in detail the net result of all is a predicted increase in the hardness and yield strength of the material. In our opinion, the use of aliovalent dopants in CdTe to form solid solutions is worthy of investigation. Typical dopants to be added include Si, Ge, As, Sb and Sn.

The above set of experiments may also prove to be beneficial to the void formation problem mentioned in a previous section. If one of the dopants were to alter free energy of formation of facets or of slow growing planes which are thought to contribute to void formation, then perhaps the problem could be solved.

* Aliovalent refers to cation additions which have a different valence than the cation present in the compound in question. In CdTe, for example, Cd^{+2} is the cation. Aliovalent cation additions to this compound would have a valance of +1, +3, +4, etc.

D. Hardness and Strength Increase by Precipitation Hardening

Precipitation hardening is used quite extensively to obtain high strength in metals. In this technique an alloy (a solid solution) is initially made. The material is then heat treated at a temperature below which the alloy was formed and the minor phase begins to precipitate from the alloy. The process occurs in several steps, but in general the greatest hardening effect is observed during the coherent precipitation stage since this produces the greatest amount of elastic strain in the lattice. In general, the yield stress for precipitation hardening tends to follow an inverse square root dependence on inter-particle spacing.

Precipitation hardening has been observed in several alkali halide systems. Yield strength on the order of 15,000 psi have been observed in KCl-NaCl alloys with both single and polycrystalline materials and it is theorized that it will also be an effective hardening mechanisms for cadmium telluride. To insure that scattering is not a problem, at all the wavelengths of interest the particle size of the precipitate must be kept below $0.1 \mu\text{m}$. Typical additives that can be added to cadmium telluride include germanium, silicon, arsenic, antimony, tin and gallium.

REFERENCES

1. J. Kiefer and A. Yariv, Appl. Phys. Letters, 15, 26 (1969)
2. K. Zanio, J. Neeland, and H. Montano, IEEE Trans. NS-17, 287 (1970).
3. P. Siffert and A. Cornet, ed., Proceedings of the International Symposium on Cadmium Telluride, Centre de Recherches Nucleaires, Strasbourg, France (1971).
4. A. J. Strauss, Ibid, p. I-1.
5. D. deNobel, "Phase Equilibria and Semiconducting Properties of CdTe, " Philips Res. Reports 14, 361 (1969).
6. F. A. Horrigan, T. F. Deutsch, "Research in Optical Materials and Structures for High-Power Lasers, Final Technical Report, Contract No. DAAH01-70-C-1251 (September 1971).
7. S. Yamada, Y. Kawasaki and O. Nishida, "Free Carrier Absorption in n-Type CdTe Crystals," Phys. Stat. Solidi 26, 77 (1968); B. M. Vul, V. M. Sal'man, V. A. Chapin, "Infrared Absorption of Spectra of p-Type CdTe," Sov. Phys. Semiconductors 4, 52 (1970).
8. B. Siegal, F. Wald, H. E. Bates, "Sonic Casting of CdTe for High-Power IR Laser Windows," Tech. Report AFML-TR-72-208, USAF Aerosystems Command, WPAFB (September 1972).
9. H. Schafer, Z. Anorg. Chem. 286, 221 (1957); R. Nitsche et al., J. Phys. Chem. of Solids 21, 199-205 (1961).

10. W. Akutagawa and K. Zanio, J. Crystal Growth 11, 191 (1971).
11. O. Tufte, First Quarterly Report, "Intrinsic Infrared Detector Development," October 1966, ARPA Contract No. F33615-67-C-1069.